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INVESTIGATIONS ON THE COMPOSITION OF PETROLEUM.

BY CHARLES F. MABERY.

XXXV.—ON THE COMPOSITION OF CALIFORNIA PETROLEUM.[1]

BY CHARLES F. MABERY AND EDWARD J. HUDSON.

In its composition as a natural product, California petroleum is the most interesting of any of the numerous petroleums that have come under our observation. When its constituents are more fully understood they will doubtless throw new light on the origin of petroleum, from the fact that they have been subjected to less rigorous agencies during, or subsequent to, their formation than petroleums from other well-known fields. In fields not yet developed, such as those of South America and Japan, similar unstable oils are found. It is useless to attempt to separate from these peculiar oils their individual constituents by the ordinary method of fractional distillation under atmospheric pressure. Not only on account of the high boiling-points, but because the presence of air causes such decomposition, hydrocarbons boiling above

[1] Presented to the American Academy of Arts and Sciences, November, 1900. Aid in the work described in these papers was given by the Academy from the C. M. Warren Fund for Original Research.

200° cannot be separated in a pure form without the aid of a vacuum. With no further knowledge of the constituents of the crude oils, this explains the numerous ineffectual attempts during the last thirty years to obtain acceptable refined products from California petroleum. By excluding air, as in vacuum distillation, with the reduction of boiling-points, it is possible to distil without decomposition all the hydrocarbons of the crude oils. With some modifications of the apparatus employed in vacuum distillation of the higher fractions of Pennsylvania oil, the fractional separation may be carried on with little more delay than in distillation under atmospheric pressure. Provision for drawing in fresh fractions without loss of vacuum may be made by sealing on a second tube to the neck of the flask a little lower than the exit tube for the escaping vapors. Then, as in the ordinary application of the Hempel principle, the cooling space in the neck of the flask may be increased by filling it with broken glass. This requires a long-necked flask, and the beads may be supported on a piece of glass rod resting on the bottom of the flask, the upper end flattened so as nearly to fill the neck of the flask as a support to the broken glass. The chief hindrance to the use of beads is the condensation of liquids with high boiling-points in the neck of the flask, due to the cooling effect of the outside air. The neck of the flask must, therefore, be packed an inch or more thick with asbestos. With this arrangement, and with a flat perforated ring burner for heating, the distillation may be conducted with a fairly rapid fractional separation, without decomposition even of the constituents that distil above 350°, 50 mm.

This examination of California oil was undertaken with the intention of ascertaining the series of hydrocarbons which constitute the main body of the crude oil, as well as the principal members of the series, as shown by percentage composition and molecular weights.

The first specimen of crude oil was received through the kindness of Mr. C. A. Black, chemist in an oil company in Ventura County. The second specimen came from a well of the Coalinga Oil Company in Fresno, through the secretary of the company, Mr. Henderson Hayward. These two speci-

mens will be referred to respectively as Ventura oil and Fresno oil. Another specimen was received from the Puente Hills in Los Angeles County, through the kindness of the Puente Oil Company at Chino. This oil will be referred to as Puente oil. Four other specimens were received from the Torrey wells and the "Los Angeles" wells in the Sespe district (Scott's Hill) in Ventura County, through the kindness of the Union Oil Company, at Santa Paula. These samples will be designated respectively as Adams' Cañon, Bardsdale, Scott's Hill, and Torrey oils.

Another specimen is of especial interest, since it came from a well sunk beneath the Pacific Ocean at high tide. It was sent by Mr. J. B. Treadwell from a well at Summerland, Santa Barbara County, at a point where the oil strata outcropped on a north and south line at the top of an elevation, and again descending on the south side, disappeared under the ocean. The well was driven to a depth of 245 feet, just within the shore line at high tide, where it reached the bottom of the oil sand. This oil will be referred to as Santa Barbara oil.

This collection of specimens seemed to offer a fair average of the oils from the California fields, representing four different counties, and deposits that yield oil in considerable quantities.

Since these crude oils differed essentially in their appearance and in their physical properties, in ascertaining their composition it seemed advisable to examine them individually.

In the spring of 1897 an examination of the Ventura oil was begun,[1] and besides giving the composition of the crude oil, the fractional separations were carried far enough *in vacuo* to identify the principal constituents boiling below 175°. The several hydrocarbons homologous with benzene, which have been found in petroleum from other sources, were found to constitute a large part of the unpurified distillates; but the chief constituents were shown by their composition and specific gravity to be methylenes, for the first time recognized as essential constituents of American petroleum.

[1] This JOURNAL, 19, 796 (1897).

PETROLEUM FROM FRESNO COUNTY.

A brief account of the composition of a specimen of crude oil from Fresno County was given in the preliminary paper referred to above. When this oil was subjected to distillation it was evident that decomposition could only be prevented in the fractions above 150° by collecting them *in vacuo*. The portion collected below 150° (atmospheric pressure) —2090 grams—was submitted to long-continued fractional separation within 1° until 50 grams collected below 55°, and only 5 grams between 55° and 68°. At 68° to 70° the distillates amounted to 60 grams, which was separated for the most part at 68°. The specific gravity of the crude distillate at 68° was found to be 0.6913, and, after thorough agitation with fuming sulphuric acid, 0.6844. A combustion of the purified oil gave the following percentages of carbon and hydrogen :

0.1692 gram of the oil gave 0.5234 gram CO_2; and 0.2314 gram H_2O.

	Calculated for C_6H_{14}.	C_6H_{12}.	Found.
C	85.70	83.72	84.38
H	14.30	16.28	15.30

The loss in this analysis is doubtless due to an escape of a very small amount of gaseous decomposition-products without complete combustion. Combustion of such a volatile oil requires the closest attention in manipulation to avoid loss in transferring to the combustion tube, and, as will appear later, the highest temperature that the hardest tube will stand is necessary for complete combustion. These results seem to indicate that the oil was a mixture of hexane and hexamethylene. The slight change in specific gravity after treatment with fuming sulphuric acid and potassic hydrate shows that the benzene had been almost completely removed. The fractions at 68° appear to be the last in California oil containing members of the series C_nH_{2n+2}. Since small quantities of distillates collected in the vicinity of 60°, 38°, and in one specimen at 30°, it is probable that the very light gasoline from California oil has the same composition as that from Pennsylvania oil.

The specific gravity of hexane, 0.6630 at 18°, and of hexa-

methylene, 0.690, also indicate that the fraction 68°–70° is a mixture of these two hydrocarbons.

Heptamethylene, C_7H_{14}.

The distillate collected at 96° to 98° amounted to 50 grams. Before purification, it gave as its specific gravity 0.7499, and after purification 0.7413. The specific gravity of heptane boiling at this point is 0.6440 (20°.5). Beilstein and Kurbatoff gave 0.742 at 18° as the specific gravity of heptanaphthene. A combustion gave the following percentages of carbon and hydrogen :

0.1413 gram of the purified oil gave 0.4442 gram CO_2; and 0.1814 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.74
H	14.30	14.35

A determination of the vapor density of the fraction 96°–98° by collecting the vapor over mercury, gave a value corresponding to the molecular weight of heptamethylene. The determination was made by the method of V. Meyer, *in vacuo*, essentially according to the modification of Lunge and Neuberg :[1]

0.0494 gram of the oil gave 22.9 cc. under a tension of 373 mm. and at 24°.

Calculated for C_7H_{14}.	Found.
3.40	3.40

The high specific gravity of this hydrocarbon corresponding to that of heptanaphthene, the composition given by analysis and the molecular weight, leave no doubt that this body is a heptamethylene, and that heptane is not contained in California (Fresno County) petroleum.

Benzene.

The distillates in the vicinity of 80°, especially at 79° to 81°, gave the characteristic odor of benzene. 20.5 grams of these fractions, shaken below 60° with a mixture of nitric and sulphuric acids, gave a heavy nitro-product; after washing with

[1] Ber. d. chem. Ges., 1891, 789.

water and distilling, the distillate weighed 13 grams, showing that 35.5 per cent of this oil was benzene. Some of the same fractions, treated with fuming nitric acid, deposited needle-shaped crystals that melted at 89°–90°, the melting-point of dinitrobenzene.

Toluene.

After the twelfth distillation, 60 grams collected at 109°–110° with the penetrating odor of toluene. Thirty grams of this distillate was shaken with a mixture of nitric and sulphuric acids, and the oil not nitrated separated from the nitro-product by distillation. The distillate weighed 13 grams, showing that 54 per cent of the original distillate was toluene. Upon agitating this product with fuming sulphuric acid and distilling, 1.6 per cent more was removed. The remaining oil was dried over sodium for analysis.

The unpurified distillate gave the following values on analysis:

0.1584 gram of the oil gave 0.5090 gram CO_2; and 0.1663 gram H_2O.

	Calculated for Toluene.	Calculated for C_nH_{2n}.	Found.
C	91.31	85.70	87.64
H	8.69	14.30	11.73

The change in composition by treatment with acids was very marked:

0.1725 gram of the purified oil gave 0.5387 gram CO_2; and 0.2282 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.20
H	14.30	14.71

Evidently the small quantity of oil remaining after the treatment with acids was octonaphthene, that had not been completely separated by distillation.

Octonaphthene, C_8H_{16}.

After the twentieth distillation, 30 grams collected at 118°–120°, which, with no further purification than drying over sodium, gave 0.7615 as its specific gravity at 20°, and, on analysis, values required for octonaphthene:

0.1457 gram of the oil gave 0.4566 gram CO_2; and 0.1922 gram H_2O.

C	85.47
H	14.71

After thorough treatment with fuming sulphuric acid the specific gravity was reduced to 0.7532 at 20° (octonaphthene, 0.7582 at 17°.5, Beilstein and Kurbatoff), but the composition was scarcely changed:

I. 0.1471 gram of the oil gave 0.4618 gram CO_2; and 0.1895 gram H_2O.

II. 0.1334 gram of the oil gave 0.4185 gram CO_2; and 0.1762 gram H_2O.

	Calculated for C_nH_{2n}.	Found. I.	Found. II.
C	85.70	85.62	85.54
H	14.30	14.32	14.67

After the eighteenth distillation, 25 grams remained persistently at 124°–125°, which was not affected by fuming sulphuric acid in the cold, but at 100° the acid became colored and gave off much sulphur dioxide. On pouring into water, the solution gave a peculiar odor resembling turpentine, and a black powder separated that contained nitrogen. Analysis of the distillate, after the treatment with the acid, gave values required for C_nH_{2n}:

0.1391 gram of the oil gave 0.4354 gram CO_2; and 0.1875 gram H_2O.

	Required for C_nH_{2n}.	Found.
C	85.70	85.36
H	14.30	14.98

Since no other hydrocarbon than normal octane has been recognized with this boiling-point, this distillate must be a mixture of octonaphthene with a higher body, but evidently normal octane is not present in appreciable quantity.

Nononaphthene, C_9H_{18}.

A considerable quantity of distillate collected at 134°–135°, that gave as its specific gravity 0.8175. After purification with fuming sulphuric acid its specific gravity was re-

duced to 0.7591. Twenty-eight grams of the crude distillate gave 13 grams of the purified oil with a loss of 53 per cent. The purified oil gave, by the action of fuming nitric acid, a nitro-derivative that, after crystallization from glacial acetic acid, melted at 85°. The melting-point of dinitromesitylene is 86°. A combustion of the purified distillate gave values for carbon and hydrogen required for nononaphthene :

0.1382 gram of the oil gave 0.4318 gram CO_2; and 0.1827 gram H_2O.

	Calculated for C_9H_{18}.	Found.
C	85.70	85.21
H	14.30	14.68

Xylenes.

Since para- and metaxylenes have frequently been found in petroleum, it did not seem advisable to separate the isomeric xylenes, although the distillates 137°–140° gave the strong penetrating odor of these bodies. At the end of the thirteenth distillation, 630 grams collected within these limits. On treating 125 grams of this product with a mixture of nitric and sulphuric acids, and agitating below 60°, washing with sodic hydrate and water, drying and distilling, only 50 grams came over below 145°, showing that the xylenes formed 60 per cent of the original distillates and had been removed as nitro-products. At the low temperature of the nitration only the aromatic hydrocarbons could have been affected. The change in composition by the nitration is shown by the following analyses :

0.1469 gram ofthe unpurified oil gave 0.4770 gram CO_2; and 0.1495 gram H_2O.

	Calculated for xylene.	Found.
C	92.31	88.53
H	7.69	11.31

Analysis of the purified distillate gave the following results on analysis :

I. 0.1382 gram of the oil gave 0.4318 gram CO_2; and 0.1827 gram H_2O.

II. 0.1386 gram of the oil gave 0.4318 gram CO_2; and 0.1837 gram H_2O.

III. 0.1441 gram of the oil gave 0.4492 gram CO_2; and 0.1901 gram H_2O.

	Calculated for C_nH_{2n}.	Found. I.	II.	III.
C	85.70	85.21	84.96	85.00
H	14.30	14.69	14.72	14.66

The chief portion of the nitrated oil was shown to be metaxylene, since the nitro-compound distilled at 240°–260°, and with fuming nitric acid it was converted into a crystalline powder insoluble in alcohol; crystallized from glacial acetic acid, it melted at 176°, the melting-point of trinitrometaxylene. Probably the 50 grams not nitrated was for the most part nononaphthene.

Nonane.

Since considerable quantities of distillates collected in the vicinity of 150°, after the seventeenth distillation, attempts were made to ascertain whether nonane is a constituent of California petroleum. This seemed of especial importance since nonane forms such an important constituent of Pennsylvania petroleum. Without purification a combustion showed the following proportions of carbon and hydrogen: Carbon, 86.14; hydrogen, 12.67. The specific gravity was 0.8117. After agitating several times with fuming sulphuric acid, the composition was materially changed:

0.1719 gram of the oil gave 0.5372 gram CO_2; and 0.2206 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.20
H	14.30	14.26

The principal constituent of this fraction was therefore a naphthene, probably hexahydrocumene.

Dekanaphthene, $C_{10}H_{20}$.

At the end of the seventeenth distillation, the quantity of distillates within 1° limits between 159° and 163° amounted to 150 grams. By further distillation these came together for the most part at 160° to 161°. The specific gravity of the unpurified distillate at 20° was 0.8272. When agitated in the

cold with fuming sulphuric acid, this distillate developed great heat; after treatment several times, until the acid was no longer much colored, the product was washed with sodic hydrate and water, and dried for analysis. The original distillate lost 75 per cent of its weight by this treatment. The aromatic hydrocarbon doubtless consisted, for the most part at least, of ethyltoluene, boiling-point 161°–162°, but no further attempts were made to identify it.

The specific gravity of the residual oil was 0.7841, practically the same as the specific gravity of dekanaphthene, 0.783, separated by Markownikoff and Oglobin from Baku petroleum. Its odor is precisely similar to that of the corresponding hydrocarbon which one of us (Mabery) has separated from crude Baku oil.

Analysis of the unpurified distillate gave the following values:

I. 0.1462 gram of the oil gave 0.4724 gram CO_2; and 0.1524 gram H_2O.

II. 0.1496 gram of the oil gave 0.4844 gram CO_2; and 0.1564 gram H_2O.

	I.	II.
C	88.10	88.28
H	11.57	11.61

After treatment with the acid the composition was materially changed; the results correspond closely to the composition of dekanaphthene:

0.1481 gram of the oil gave 0.4646 gram CO_2; and 0.1932 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.55
H	14.30	14.50

A determination of the molecular weight gave a value required for dekanaphthene.

0.8850 gram of the oil and 24.22 grams benzene gave, by the Beckmann method, at the freezing-point, a depression of 1°.28.

Calculated for $C_{10}H_{20}$.	Found.
140	140

After the twenty-fourth distillation, 50 grams collected at 169°–170°, which gave as its specific gravity without purification, 0.8358. After thorough agitation with fuming sulphuric acid and washing, the specific gravity was reduced to 0.7749, but the larger portion of the oil was removed by the acid, indicating that the fraction consisted for the most part of a benzene homologue. The small quantity remaining after the treatment was doubtless dekanaphthene, since its specific gravity was nearly the same.

The presence of a naphthene in Russian oil, boiling at 182°, led us to believe that the same body should be found in California oil; but the small quantity of distillate collecting here, only 10 grams after long distillation, excluded this hydrocarbon in any appreciable quantity.

Undekanaphthene, $C_{11}H_{22}$ (195°).

Between 188° and 191°, 50 grams came together at the end of the tenth distillation, which gave the following results on analysis:

0.1423 gram of the oil gave 0.4550 gram CO_2; and 0.1617 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	87.20
H	14.30	12.63

The specific gravity of this distillate before treatment was 0.8386. After vigorous agitation with fuming sulphuric acid, and washing, the specific gravity was reduced to 0.8044.

A distillate separated from Russian oil at 197° gave (Markownikoff and Oglobin) as its specific gravity at 14°, 0.8055, and it was assigned the formula $C_{13}H_{24}$. The quantity of oil remaining after separation of durene, which no doubt was the benzene hydrocarbon in this distillate, was small. That it was a naphthene, as shown by its specific gravity, is confirmed by analysis.

0.1459 gram of the oil gave 0.4575 gram CO_2; and 0.1886 gram H_2O.

	Calculated for $C_{13}H_{24}$.	Found.
C	85.70	85.70
H	14.30	14.40

Determinations of the molecular weight of this fraction by the Beckmann freezing-point method, using benzene, gave the following value:

0.7901 gram of the oil and 24.68 grams benzene gave a depression of 1°.012.

1.1249 gram of the oil and 25.90 grams benzene gave a depression of 1°.36.

Calculated for $C_{11}H_{22}$.	Found.	
	I.	II.
154	155	157

It appears from these results that the hydrocarbon in California petroleum boiling at 195° is not dodekanaphthene, $C_{12}H_{24}$, but undekanaphthene, $C_{11}H_{22}$. This conclusion is further confirmed, as will appear later, by the composition of the distillate 216°, which appears to be dodekanaphthene, and still further by the composition of the monochlornaphthene obtained from the hydrocarbon boiling at 195° which gives as its formula $C_{11}H_{21}Cl$.

In the vicinity of 200°, 50 grams of a distillate collected which gave as its specific gravity 0.8684. After agitation with fuming sulphuric acid, the specific gravity was diminished to 0.8202. An analysis before treatment gave 87.84 per cent of carbon and 11.91 per cent of hydrogen. After treatment with the acid, the analysis gave 85.99 per cent of carbon and 13.97 per cent of hydrogen, showing that some of the aromatic hydrocarbon still remained; the small amount of naphthene was doubtless undekanaphthene, boiling at 195°; sp. gr. 0.8010, as given above.

Dodekanaphthene, $C_{12}H_{24}$.

A considerable quantity of distillate collected at 208° to 210°, corresponding to 216°, which corresponded in composition by analysis and molecular weight to dodekanaphthene:

0.1496 gram of the oil gave 0.4677 gram CO_2; and 0.1962 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.26
H	14.30	14.57

Determinations of the molecular weight of this product by the Beckmann method at the freezing-point, gave results corresponding to the formula of dodekanaphthene.

1.0141 grams of the oil and 25.61 grams benzene gave a depression of 1°.17.

Calculated for $C_{12}H_{24}$.	Found.
166	166

It is therefore evident that California petroleum differs from Russian oil in containing dodekanaphthene, boiling at 216°, as well as undekanaphthene, boiling at 195°.

Puente Oil.

The specimen received from the Puente Oil Company was somewhat thicker than the Fresno oil. Its specific gravity at 20° was found to be 0.892. It contained 0.80 per cent of sulphur. Two determinations of nitrogen by the Kjeldahl method gave : (I) 0.564, (II) 0.587 ; and by the absolute method, measuring the volume of nitrogen, (I) 1.18, and (II) 1.22. A combustion of the crude oil gave 84.96 per cent of carbon and 11.96 per cent of hydrogen. Two determinations of bromine absorption gave : (I) 18.8, and (II) 18.3 per cent.

A distillation of 1346 grams of the crude oil, under atmospheric pressure, gave the following weights :

Below 100°.	100°–150°.	150°–200°.	200°–250°.
167	170	132	130 grams

The small proportions distilling below 250° made it evident that the chief constituents could only be separated *in vacuo*. The specific gravity of these distillates at 20° were ascertained by weighing on a Westphal balance :

100°.	100°–150°.	150°–206°.
0.7642	0.8155	0.8538

Ten liters of the Puente crude oil, after collecting below 150° at atmospheric pressure, gave the following weights under 50 mm :

150 at. pr.	Below 120°.	120°–150°.	150°–175°.	175°–185°.	185°–200°.
590	800	827	990	160	495 grams

The residue above 200° was next divided into fractions of convenient size, without noting temperatures :

1.	2.	3.	4.
655	1010	670	430 grams

Further distillation of the fraction –150 atmospheric pressure gave the following weights :

Below 60°.	60–62°.	66°–68°.	78°–82°.	88°–90°.	96°–98°.	109°–110°.	118°–120°.
10	10	10	27	40	120	60	65 grams

Smaller weights collected at intermediate temperatures.

Heptamethylene, C_7H_{14}.

No attempts were made to ascertain the composition of the individual fractions below 96° from Puente oil. Those portions will receive further attention with the corresponding distillates from the other oils. Without purification the distillate 96°–98° gave as its specific gravity at 20°, 0.7499. After repeated agitation with fuming sulphuric acid and potassic hydrate the specific gravity was scarcely changed, 0.7440; specific gravity of heptanaphthene, 0.742 at 18°. Analysis I. was made of the untreated oil, Analysis II. of the portion after treatment :

I. 0.1409 gram of the oil gave 0.4438 gram CO_2 ; and 0.1683 gram H_2O.

II. 0.1396 gram of the oil gave 0.4383 gram CO_2; and 0.1792 gram H_2O.

	Calculated for C_7H_{14}.	Found. I.	II.
C	85.70	85.90	85.60
H	14.30	13.27	14.26

The difference in Analysis I. is doubtless due to oxygen and nitrogen compounds, since agitation of the crude distillates with potassic hydrate separates from most of the distillates from California petroleum heavy oils, with an odor resembling that of creosote. A description of these oxygenated compounds is reserved for a later paper. The specific gravity of the purified fraction, 0.7440, is essentially the same as that of heptanaphthene separated from Russian oil, 0.748, by Beilstein and Kurbatoff.

Octonaphthene, C_8H_{16}.

The fraction 118°–120°, without further treatment, gave as

its specific gravity at 20°, 0.7615, which was reduced to 0.7540 by agitation with fuming sulphuric acid. Specific gravity of octonaphthene, 0.7552 at 17°.5. Analysis I. was made of the crude distillate, and Analysis II. of the oil after purification with the acid:

I. 0.1406 gram of the oil gave 0.4424 gram CO_2; and 0.1760 gram H_2O.

II. 0.1503 gram of the oil gave 0.4692 gram CO_2; and 0.1941 gram H_2O.

	Calculated for C_8H_{16}.	Found. I.	Found. II.
C	85.70	85.81	85.20
H	14.30	13.91	14.35

No further examination was made of the fractions from 120° to 140°, but it seemed of interest to ascertain whether nonane formed any part of the distillate 148°–150°, since it forms such a large proportion of the Eastern oils. The crude distillate 150°–151° gave as its specific gravity 0.7910, and after purification with sulphuric acid, 0.7730. Analysis of the treated oil gave percentages of carbon and hydrogen that still showed the presence of the benzene homologue.

0.1449 gram of the oil gave 0.4589 gram CO_2; and 0.1807 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	86.37
H	14.30	13.57

From the results of this analysis it is evident that nonane forms no appreciable proportion of Puente oil.

Dekanaphthene, $C_{10}H_{20}$.

Fifty grams of a distillate collected at 160°–162°, with smaller quantities on either side. A determination of its specific gravity at 20° gave 0.7966, and after agitation with sulphuric acid, 0.7745. The composition of this distillate after treatment with the acid was shown by analysis:

0.1747 gram of the oil gave 0.5515 gram CO_2; and 0.2185 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	86.09
H	14.30	13.90

Fraction 168°–172°.

In all the California oils examined, as stated above, considerable quantities have collected at 168°–172°. Since large proportions of the benzene hydrocarbons appear in all these oils, the distillate 168°–172° might exist to a large extent of pseudocumene, boiling-point 168°. The high specific gravity of the fraction before treatment with the acid, 0.8063, and the lower value after treatment, 0.7874, indicates a considerable proportion of the benzene homologue. Even after the acid treatment, the percentages of carbon and hydrogen showed the presence still of the same constituent: carbon, 85.91; hydrogen, 13.61. It seems probable, therefore, that the benzene homologue constitutes the greater part of this distillate, and the residue, after treatment, is doubtless higher or lower constituents; but the absence of a decane corresponding to the decane in Pennsylvania petroleum, boiling at 172°, is assured.

Fraction 180°–182°.

Only 10 grams collected at 180°–182°, with smaller quantities on either side. Although this quantity of the oil was insufficient for complete examination, its specific gravity before and after analysis was ascertained, and an analysis made after treatment with acid. Before treatment the value obtained was 0.8116, and afterward 0.7955. A combustion gave 86.27 per cent of carbon, and 13.79 per cent of hydrogen. Evidently, like the Fresno oil, Puente oil has no constituent with this boiling-point, except a benzene homologue.

Undekanaphthene, $C_{11}H_{22}$ (195°).

A naphthene should be expected between 190° and 200°, since undekanaphthene, $C_{11}H_{22}$, is a constituent of the Fresno oil. The 20 grams collecting at 190°–192° gave as its specific gravity at 20°, 0.8196, and after treatment with fuming acid, 0.8046 (0.8055 at 14°, Markownikoff). A combustion of the oil after treatment gave 85.90 per cent of carbon and 13.85 per cent of hydrogen.

The series C_nH_{2n+2} forms no part of the Puente oil, at least above 95°. The low percentage of hydrogen seems to indicate a series still poorer in hydrogen than the naphthenes, especially in the higher distillates, possibly a series C_nH_{2n-2}, containing two naphthene rings. Whether such hydrocarbons are really present, or whether benzene homologues have not been completely removed, will appear in more prolonged distillation of these oils boiling above 200°.

BARDSDALE OIL.

The specimen marked "Owens No. 2," sent by the Union Oil Co. from the Bardsdale district, was quite thick and heavy. Its specific gravity at 20° was 0.8923. It contained 1.25 per cent of nitrogen, as shown by the volume of nitrogen collected. A Kjeldahl determination gave 0.50 per cent. A Carius determination gave 1.5 per cent of sulphur, showing it to be a high sulphur oil. A combustion gave 84.17 per cent of carbon and 12.15 per cent of hydrogen. 108 grams of the oil distilled under atmospheric pressure gave the following weights:

Below 150°.	150°–310°.	310°–410°.
9	24	7 grams
0.7433	0.8170	Specific gravity

In distilling 5088 grams under 50 mm., except –150°, the following weights were obtained:

Below 150° at. pr.	150°–200°.	200°–250°.	250°–290°.
250	555	374	1165 grams

The two fractions below 200° were distilled within 5°, and then within 2°, which brought together the following weights with smaller quantities at neighboring temperatures:

96°–100°.	116°–120°.	136°–140°.	148°–150°.	158°–162°.	168°–172°.	190°–194°.
34	25	35	40	60	20	40 grams

The lower portions of this oil began to come over at 45°, but only small quantities collected below 65°. At 65°–70°, 40 grams collected, which will be examined in connection with the similar distillates from the other oils to ascertain whether the principal constituent is hexane or hexamethylene. The high specific gravity of this oil, even after treating thor-

oughly with fuming sulphuric acid, 0.7017, would seem to exclude hexane, sp. gr. 0.6671.

Heptamethylene, C_7H_{14}.

The unpurified fraction, 96°–100°, gave as its specific gravity at 20°, 0.7395, and after treatment with fuming acid, 0.7384. The slight change in specific gravity indicates that this fraction consists for the most part of one hydrocarbon, and analysis with the boiling-point shows that the hydrocarbon is heptamethylene, sp. gr. 0.7420.

0.1473 gram of the oil gave 0.4620 gram CO_2; and 0.1879 gram H_2O.

	Calculated for C_7H_{14}.	Found.
C	85.70	85.54
H	14.30	14.18

Octonaphthene, C_8H_{16}.

The specific gravity of the fraction 116°–120° was 0.7625, and after treatment with fuming sulphuric acid, 0.7566, which indicated that this product contained very little of the benzene homologues. An analysis, after purification, gave proportions of carbon and hydrogen required for octonaphthene:

0.1780 gram of the oil gave 0.5572 gram CO_2; and 0.2287 gram H_2O.

	Calculated for C_8H_{16}.	Found.
C	85.70	85.39
H	14.30	14.28

Fraction 150°–152°.

The distillates above 120° received no further attention, except to ascertain that the xylols were present in large proportion, as in the other oils. To ascertain whether nonane is contained in this oil, the specific gravity of the fraction 150°–152° was ascertained and found to be 0.7756, after treatment with the fuming acid. Its composition, after treatment with the acid, corresponded to that of C_nH_{2n}:

0.1434 gram of the oil gave 0.4480 gram CO_2; and 0.1839 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.20
H	14.30	14.25

The lower specfic gravity of nonane and the results of analysis show that nonane is not a constituent of this oil.

Dekanaphthene, $C_{10}H_{20}$.

The specific gravity of the unpurified fraction 160°–162° at 20° was 0.7966, and after purification with fuming sulphuric acid and sodic hydrate was 0.7905 ($C_{10}H_{20}$, 0.7950 at 0°, Markownikoff).

It gave the following results on analysis:

I. 0.1471 gram of the oil gave 0.4625 gram CO_2; and 0.1907 gram H_2O.

II. 0.1475 gram of the oil gave 0.4477 gram CO_2; and 0.1813 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found. I.	Found. II.
C	85.70	85.50	85.86
H	14.30	14.37	14.17

On account of the small amount of the distillate 167°–170°, no examination was made of it. It was doubtless chiefly a benzene homologue.

Fraction 176°–178°.

To ascertain whether a naphthene boiling at 182° is present in this oil, the fraction 176°–178° was treated thoroughly with fuming sulphuric acid and sodic hydrate. Its specific gravity before treatment was 0.8116; after treatment, 0.7955. It gave, on analysis, 86.01 per cent carbon and 13.31 per cent hydrogen, indicating still the presence of a benzene homologue. But the small quantity remaining showed the absence of any other constituents with this boiling-point in this distillate.

Undekanapthene, $C_{11}H_{22}$.

The fraction 190°–194° gave 0.8186 as its specific gravity before treatment with fuming sulphuric acid and sodic hydrate, and afterward 0.8046. Markownikoff found 0.8119 at 0° as the specific gravity of dodekanaphthene from Baku oil.

The percentages of carbon and hydrogen given by analysis supported the formula of undekanaphthene:

0.1466 gram of the oil gave 0.4588 gram CO_2; and 0.1909 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	85.37
H	14.30	14.47

Some of the Bardsdale distillates, 140°–220°, 50 mm., turned pink soon after they were collected, changing to a darker red on standing, and after some time they deposited a dark oil. The colored distillates alternated with the others, leaving sharply-lined uncolored oils besides those depositing the insoluble heavy oils. The following distillates were colored:

154°–156°, 158°–160°, 168°–170°, 180°–182°, 198°–206°, 212°–216°.

The distillates between these were nearly or quite colorless. This coloration was caused by the phenol bodies, which are easily extracted by alkaline hydrates. The bodies will receive further attention in another paper.

ADAMS CAÑON OIL.

The Adams Cañon Oil from the Ex-Mission district was thicker and heavier than the oils previously described. The specific gravity of this specimen at 30° was 0.9212. It contained a large percentage of nitrogen, 1.46, determined by the volume of nitrogen. The Kjeldahl method gave 0.58 per cent. Two determinations of sulphur gave: (I) 0.92; (II) 0.87. This oil contained a very small proportion of the lower hydrocarbons. 100 grams distilled under atmospheric pressure gave 8 grams below 150°, and 27 grams, 150°–300°. The specific gravity of the lower distillate was 0.7673, and of the higher 0.8457. In vacuum distillation, 9382 grams of the crude oil gave the following weights:

Below 150° at. pr.	–120°.	120°–160°.	160°–250°.
123	865	1045	525

Nearly three-fourths of the original oil remained above 250°.

Continuing the distillation of the lower distillates within 5° and 2°, the following weights were collected:

96°-100°.	116°-120°.	158°-160°.	168°-170°.	180°-182°.
37	10	12	20	10 grams

In continuing the distillation of the lower fractions nothing came over below 60°, and only in quantities of a few grams below 95°.

Heptamethylene, C_7H_{14}.

The fraction 98°–100° unpurified gave as its specific gravity at 20°, 0.7444, and after treatment with fuming sulphuric acid and sodic hydrate, 0.7414. A combustion of the purified oil gave the following percentages of carbon and hydrogen:

0.1525 gram of the oil gave 0.4797 gram CO_2; and 0.1976 gram H_2O.

	Calculated for C_7H_{14}.	Found.
C	85.70	85.53
H	14.30	14.40

As in the other oils, much benzene was contained in the fractions near 80°, and toluene in those near 110°.

Octonaphthene, C_8H_{16}.

The fraction 118°–120° gave as its specific gravity unpurified at 20°, 0.7632, and after treatment with fuming acid and sodic hydrate, 0.7600. Specific gravity of octonaphthene, 0.7582. This distillate gave, after purification, 86.52 per cent of carbon, and 14.60 per cent of hydrogen, which with its boiling-point showed it to be octonaphthene.

To ascertain whether nonane is a constituent of Adams Cañon oil, the specific gravity of the distillate 148°–150° was determined, and found to be 0.7858. After treatment with the fuming acid and sodic hydrate its specific gravity was but slightly changed, 0.7800. A combustion then gave 86.10 per cent of carbon and 13.91 per cent of hydrogen.

Since nonane requires 84.37 per cent of carbon and 15.63 per cent of hydrogen, it is evident that this hydrocarbon is not a constituent of Adams Cañon oil.

Dekanaphthene, $C_{10}H_{20}$.

The unpurified distillate 158°–160° gave as its specific gravity at 20°, 0.7972, and 0.7904 after treatment with the fuming acid and sodic hydrate. A combustion of the purified oil gave the following percentages of carbon and hydrogen:

0.1455 gram of the oil gave 0.4583 gram CO_2; and 0.1804 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.91
H	14.30	13.78

The low percentage of hydrogen and high percentage of carbon indicates that the benzene homologue was not completely removed. In some of these distillates the benzene hydrocarbon is present in such large proportion that long continued action of the fuming acid is necessary to remove it completely.

The small amount of the distillate 180°–182° gave as its specific gravity, at 20°, 0.8154, and after treatment with the fuming acid, 0.8097. A combustion of the treated oil gave 85.56 per cent of carbon and 13.95 per cent of hydrogen. No further examination was made of the fractions collected under atmospheric pressure. Like the Bardsdale oil, part of the distillates between 140° and 220° under 50 mm. turned pink soon after they were collected, and on standing deposited a dark colored oil.

While the possibility of hydrocarbons poorer in hydrogen, such as condensed naphthenes, is suggested by the low percentage of hydrogen, on account of the very large proportion of aromatic derivatives of benzene contained in Adams' Cañon oil, it seems more probable that these results are due to benzene derivatives not wholly removed, especially as the boiling-points of the double-ring naphthenes undoubtedly are much higher. Such a double-ring naphthene, apparently formed as one of the products by the action of sodium on monochlorheptamethylene boiled in the vicinity of 240°.

TORREY WELLS OIL.

The specimen of petroleum from the Torrey wells was much lighter than that from Adams Cañon; its specific gravity, at 20°, was 0.8837. It contained 0.49 per cent of sulphur, and gave 0.38 per cent of nitrogen by the Kjeldahl method and 1.15 per cent by volume. A combustion gave 86.00 per cent of carbon and 12.48 per cent of hydrogen; 100 grams distilled under atmospheric pressure gave 11 grams with a specific gravity of 0.7519 below 150° and 29 grams, sp. gr. 0.8226, between 150° and 250°. In distilling Torrey oil *in vacuo*, 9860 grams gave the following weights:

Below 160° at. pr.	–125°.	125°–175°.	175°–225°.	225°–275°.
655	790	1175	900	700 grams

Further distillation of the lower fractions gave, after the fourth distillation, the following weights, with smaller proportions at temperatures between :

96°–98°.	116°–120°.	136°–140°.	158°–162°.	168°–171°.	178°–182°.
78	40	45	37	43	35 grams

The Torrey oil contained more of the lower distillates than any other of the specimens examined. Several grams collected below 40°, and at 65° to 70°, 30 grams came together. The unpurified distillate 65°–70° gave as its specific gravity, at 50° 0.6981, which was reduced only to 0.6926 after agitation with fuming sulphuric acid. The specific gravity of hexane, boiling at 68°, is 0.6630.

Analysis of the purified oil gave the following results :

I. 0.1551 gram of the oil gave 0.4768 gram CO_2; and 0.2138 gram H_2O.

II. 0.1995 gram of the oil gave 0.6146 gram CO_2; and 0.2769 gram H_2O.

III. 0.1369 gram of the oil gave 0.4248 gram CO_2; and 0.1888 gram H_2O.

	Calculated for		Found.		
	C_6H_{12}.	C_6H_{14}.	I.	II.	III.
C	85.70	83.72	83.85	83.93	84.63
H	14.30	16.28	15.32	15.41	15.33

In Analysis III. every precaution was taken to avoid loss of the oil after weighing, and the temperature of the combustion was maintained as high as the tube would stand. Probably the coincidence in the percentages of hydrogen is due to retention of unsaturated hydrocarbons in the sulphuric acid.

Apparently, as in the Fresno oil, the hydrocarbon at 68° is a mixture of hexane and hexamethylene.

Heptamethylene, C_7H_{14}.

The fraction 96°–98° had the specific gravity, at 20°, 0.7496, which was scarcely changed by treatment with fuming sulphuric acid, 0.7430. Analysis I. was made of the crude distillate, and Analysis II. of the purified product :

I. 0.1222 gram of the oil gave 0.3810 gram CO_2; and 0.1602 gram H_2O.

II. 0.1530 gram of the oil gave 0.4801 gram CO_2; and 0.1974 gram H_2O.

	Calculated for C_7H_{14}.	Found. I.	II.
C	85.70	84.97	85.60
H	14.30	14.56	14.34

This product is, therefore, fairly pure heptamethylene.

The fractions in the vicinity of 110° were shown to be composed for the most part of toluene by the formation of nitro-products.

Octonaphthene, C_8H_{16}.

The specific gravity of the crude distillate 118°–120° was 0.7598, and after purification with fuming sulphuric acid and sodic hydrate, 0.7530. A combustion of the unpurified oil gave 86.21 per cent of carbon and 13.35 per cent of hydrogen.

A combustion, after purification, indicated octonaphthene, although the percentage of hydrogen is somewhat too high, probably on account of accidental moisture:

0.1470 gram of the oil gave 0.4598 gram CO_2; and 0.1976 gram H_2O.

	Calculated for C_8H_{16}.	Found.
C	85.70	85.34
H	14.30	14.93

The distillates 135°–140° consisted largely of the xylenes.

Dekanaphthene, $C_{10}H_{20}$.

The specific gravity of the crude fraction 158°–160° was 0.7742, and after purification with the fuming acid and sodic hydrate, 0.7742. Carbon and hydrogen were determined in the purified oil:

0.1455 gram of the oil gave 0.4583 gram CO_2; and 0.1804 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.91
H	14.30	13.78

Determinations of the specific gravity of the crude distillate 168°–170 gave 0.7928, and 0.7840 after treatment with fuming acid and sodic hydrate. A combustion of the purified oil gave 85.98 per cent of carbon and 13.69 per cent of hydrogen.

The fraction 178°–182° had the specific gravity before treatment, 0.8006, and afterward, 0.7924. A combustion of the oil after treatment gave 85.97 per cent of carbon and 13.51 per cent of hydrogen. The fraction 198°–200° had the specific gravity of 0.8133, and after treatment 0.8069. The following percentages were given by combustion: carbon, 86.51; hydrogen, 13.54.

The low proportions of hydrogen and high proportions of carbon alluded to before are especially apparent in the Torrey oil. Whether this be due to a higher series or to benzene homologues not easily removed will appear later in the composition of the higher vacuum distillates.

The Torrey distillates 140°–220°, 50 mm., showed a larger proportion of oxygen and nitrogen compounds than any other of the crude oils.

SCOTT'S HILL (SESPE DISTRICT) OIL.

The specimen of petroleum from Scott's Hill was lighter than the Torrey oil; its specific gravity at 20°, was 0.8782. It contained 1.25 per cent of nitrogen. Two determinations of sulphur gave (I) 0.38 and (II) 0.49 per cent. 8260 grams of the crude oil gave the following weights on distillation *in vacuo*:

Below 150° at. pr.	–160°.	160°–208°.	208°–275°.
1220	495	930	880

The distillate –150° was collected under atmospheric pressure, the others under 70 mm. The portion –150° was subjected to further distillation collecting at first within 5°, and twice within 2°. The fractions collected in larger quantities within the following limits:

66°–70°.	86°–90°.	96°–100°.	116°–120°.	136°–140°.	156°–160°.	170°–174°.	178°–182°.	190°–192°.
26	38	35	37	38	62	41	38	41

Continuing the distillation of the higher fractions *in vacuo*, after the third distillation within limits of 2°, the larger quantities collected within the following limits with smaller quanties between:

144°–148°.	164°–168°.	182°–186°.	210°–214°.
60	55	65	23

In distilling corresponding fractions from other fields *in vacuo* a tendency to collect within the same limits was observed. After agitation with fuming sulphuric acid, the fraction 66°–70°, atmospheric pressure, gave as its specific gravity, at 20°, 0.6984; a value much higher than the specific gravity of hexane, 0.6630 (17°.5). A combustion gave percentages of carbon and hydrogen corresponding to a mixture of hexamethylene and hexane:

	Calculated for C_6H_{12}.	Calculated for C_6H_{14}.	Found.
C	85.70	83.72	84.67
H	14.30	16.28	15.15

The distillates 65°–70° from Torrey, Scott's Hill, and Fresno oils were put together and carefully distilled a number of times in order to separate, so far as possible, the hydrocarbon boiling at 68° or 69° from other admixtures, and the fraction 68°–69° was thoroughly treated with fuming sulphuric acid, warming gently, and allowing it to stand with the acid over night. Before treatment the specific gravity, at 20°, was 0.7005, and after treatment 0.6929. The following results were obtained by analysis:

0.2422 gram of the oil gave 0.7596 gram CO_2; and 0.3234 gram H_2O.

	Calculated for C_6H_{12}.	Calculated for C_6H_{14}.	Found.
C	85.70	83.72	85.50
H	14.30	16.28	14.84

In this analysis the combustion tube was filled with oxygen before the oil was volatilized, and the temperature was kept as high as the tube would stand.[1] There seems, therefore, to

[1] In a paper on the determination of carbon and hydrogen by combustion, using copper oxide (J. Am. Chem. Soc., April, 1900), I mentioned as one of the essential details that the combustion tube must be heated as hot as it would stand. I have observed invariably, in the analysis even of perfectly pure substances, with the tube heated to redness, that the percentages of carbon and hydrogen came too low. I ascribed this loss to the formation of marsh gas which could not be completely burned at temperatures lower than a dull white heat. In a recent investigation on the temperatures of combustion of hydrogen and marsh gas by passing over heated copper oxide, Armand Gautier (Compt. rend. (1900), 130, (1353–1360), finds that hydrogen is completely oxidized by heating just to redness in a length of oxide less than that of a combustion tube. But methane largely diluted with air, 16 methane to 100,000 air, is only partly burned, 58.3 per cent hydrogen in the methane and 36 per cent of the carbon only were oxidized. Even in a much longer tube methane was not completely oxidized. This agrees with my experience, since with temperatures below very bright redness, even in a tube five feet long, the combustion was incomplete.—C. F. M.

be little doubt that the hydrocarbon in California petroleum boiling at 68°–69° is composed chiefly of hexamethylene.

Since small quantities of distillates remained in the vicinity of 90° to 91°, it suggested the possibility that isoheptane might form a part of this product. But its high specific gravity, 0.7303 at 20°, isoheptane 0.6819 (17°.5), and the composition showed by analysis excluded isoheptane in any considerable quantity.

0.1273 gram of the oil gave 0.3987 gram CO_2; and 0.1665 gram H_2O.

	Calculated for C_7H_{14}.	C_7H_{16}.	Found.
C	85.70	84.00	85.40
H	14.30	16.00	14.53

Special precautions were taken in this analysis to have the temperature of the combustion as hot as possible, and the tube was filled with oxygen before the oil volatilized. The proportions of carbon and hydrogen indicating the absence of isoheptane could not have been due to the presence of benzene, since the oil was treated several times with fuming sulphuric acid. The volatile portions of California petroleum, therefore, contain at most very small proportions of the hydrocarbons, C_nH_{2n+2}, and these, if present, consist almost exclusively of members below normal hexane. Further confirmation of these formulæ is given by the chlorine derivatives, which will be described in another paper.

Heptamethylene, C_7H_{14}.

The fraction 96°–98° gave as its specific gravity, at 20°, 0.7479, and after purification with fuming sulphuric acid, 0.7436. A combustion of the purified oil gave the following results:

0.1530 gram of the oil gave 0.4801 gram CO_2; and 0.1974 gram H_2O.

	Calculated for C_7H_{14}.	Found.
C	85.70	85.60
H	14.30	14.34

These values leave no doubt that this constituent was heptamethylene.

Octonaphthene, C_8H_{16}.

A determination of the specific gravity of the fraction 118°–120°, at 20° gave 0.7628, and after agitation with fuming acid and sodic hydrate, 0.7569. Determinations of carbon and hydrogen were made both before and after purification.

I. 0.1644 gram of the unpurified oil gave 0.5196 gram CO_2; and 0.1975 gram H_2O.

II. 0.1470 gram of the purified oil gave 0.4600 gram CO_2; and 0.1976 gram H_2O.

	Calculated for C_8H_{16}.	Found. I.	II.
C	85.70	86.21	85.34
H	14.30	13.35	14.93

Although all these oils were dried over sodium, the hydrogen in Analysis II. is somewhat too high, probably on account of a trace of moisture.

No further examination of the higher fractions of this oil below 160° was made, except of the portion collected at 135° to 140°, to show that large proportions of the xylenes were contained as in the other specimens examined.

Dekanaphthene, $C_{10}H_{20}$.

The specific gravity of the fraction 158°–160° was found to be 0.7848, and after agitation with the fuming acid, 0.7751. The proportions of carbon and hydrogen were determined by analysis:

I. 0.1444 gram of the oil gave 0.4575 gram CO_2; and 0.1885 gram H_2O.

II. 0.1451 gram of the oil gave 0.4533 gram CO_2; and 0.1848 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found. I.	II.
C	85.70	85.65	85.24
H	14.30	14.22	14.33

Undekanaphthene, $C_{11}H_{22}$.

The specific gravity of this fraction, without purification, was 0.8093 at 20°, and after treatment with the fuming acid and sodic hydrate, 0.7952. A combustion gave the following percentages of carbon and hydrogen:

0.1458 gram of the oil gave 0.4593 gram CO_2; and 0.1817 gram H_2O.

	Calculated for $C_{13}H_{28}$.	Found.
C	85.70	85.90
H	14.30	13.85

Assuming, which is probable, that the benzene homologue was completely removed, these proportions of carbon and hydrogen point to the presence of a hydrocarbon of a series containing less hydrogen.

A similar result was obtained with the fraction 194°–196°, specific gravity crude, 0.8145; and after treatment, 0.8022. Combustion of the purified oil gave the following percentages:

	I.	II.
C	85.52	85.85
H	13.97	13.92

While the percentages of carbon in these analyses are satisfactory for the formula C_nH_{2n}, the percentages of hydrogen are less satisfactory. The deficiency of about 0.5 per cent in the sum of the carbon and the hydrogen has appeared in many of the analyses of products that could be reasonably accepted as to their formulas. With the greatest care in the details of analysis, we have also found difficulty in obtaining the total carbonic dioxide evolved by combustion of the oil in the ordinary method of analysis. This subject has received attention in another paper on this method of analysis.

Tridekanaphthene, $C_{13}H_{26}$.

After the separation of distillates *in vacuo* from the crude oils, the fractions may be distilled at temperatures which would cause decomposition of constituents of the crude oil. It is therefore possible to continue the distillation of the hydrocarbons even as high as tridekanaphthene under atmospheric pressure after the first distillation. In continuing the distillation, 35 grams collected at 230°–232°, sp. gr. 0.8511. After purification with fuming sulphuric acid it gave as its sp. gr. 0.8134 at 20°. A combustion gave the following results:

0.1511 gram of the oil gave 0.4733 gram CO_2; and 0.1937 gram H_2O.

	Calculated for $C_{13}H_{26}$.	Found.
C	85.70	85.41
H	14.30	14.24

This formula was also verified by a determination of its molecular weight:

1.2712 grams of the oil and 25.24 grams benzene gave a depression of 1°.370.

Calculated for $C_{13}H_{26}$.	Found.
182	180

A determination of the index of refraction gave 1.4745, and the molecular refraction 60.254; calculated for $C_{13}H_{26}$, 59.839.

Tetradekanaphthene, $C_{14}H_{28}$.

A considerable quantity of distillate collected at 144° to 146°, which gave as its specific gravity before purification 0.8428, and after purification 0.8154. A combustion gave percentages of carbon and hydrogen required for the formula C_nH_{2n}.

0.1462 gram of the oil gave 0.4600 gram CO_2; and 0.1824 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.81
H	14.30	13.87

A determination of molecular weight at the freezing-point gave a value required for tetradekanaphthene:

1.3356 gram of the oil and 24.22 grams benzene gave a depression of 1°.394.

Calculated for $C_{14}H_{28}$.	Found.
196	194

The index of refraction of this hydrocarbon was found to be 1.4423, and the molecular refraction, 63.75; required for $C_{14}H_{28}$, 64.44.

Pentadekanaphthene, $C_{15}H_{30}$.

From each of the California oils, distillates *in vacuo* col-

lected at 160°–162°, 50 mm., corresponding nearly to 260° to 262°, atmospheric pressure. The specific gravity of the fraction from Scott's Hill oil was 0.8600, and after purification with fuming sulphuric acid, 0.8171. A combustion gave the following values for carbon and hydrogen:

0.1454 gram of the oil gave 0.4558 gram CO_2; and 0.1829 gram H_2O.

	Calculated for $C_{18}H_{30}$.	Found.
C	85.70	85.47
H	14.30	13.97

The percentages of carbon and hydrogen in the analysis of the two hydrocarbons last described indicate a falling off in the proportions of hydrogen. The deficiency in the analysis is more probably due to loss of carbonic dioxide than of water. Similar variations have been noted in connection with some of the lower hydrocarbons in other crude California oils. The deficiency in hydrogen may indicate, as mentioned heretofore, the presence of hydrocarbons composed with more than one methylene ring, which would require prolonged distillation for their complete removal. From the heavier California oils composed, it appears, largely of asphaltic hydrocarbons, the falling off in the proportion of hydrogen and consequent increase in carbon indicates the presence of hydrocarbons with the formula C_nH_{2n-2}. Such differences do not appear in determinations of molecular weights, but are shown by analysis.

There are wide variations in the specific gravity of the distillates of California oil above 230° from different sources. This may indicate a certain proportion of hydrocarbons of a lower series than C_nH_{2n}, and the higher percentages of carbon and lower percentages of hydrogen in some of these oils indicate the possibility of hydrocarbons C_nH_{2n-2}.

For faithful assistance in this work, the following gentlemen should receive credit: Messrs. Shaw, Ames, Richards, Cushing.

From this examination of California petroleum, the following conclusions may be drawn:

An essential characteristic is the relatively small proportions of the distillates below 225°. The main body of the

crude oils from the principal fields distilling below 225° is composed of methylenes which resemble those identified in Russian oil, in boiling-points, and in specific gravity, except undekanaphthene, $C_{11}H_{22}$, dodekanaphthene, $C_{12}H_{24}$, and tridekanaphthene, $C_{13}H_{26}$, which differ in boiling-points. The proportion of the aromatic hydrocarbons is much larger, apparently, in California oil. The homologues of benzene form a considerable proportion of the distillates, especially of those with lower boiling-points. In the distillate 221°–222° from Puente oil so much naphthalene was present that the distillate became solid at 0°.

California petroleum differs totally from the Eastern oils—Pennsylvania, Ohio, Canadian, etc.—and also materially from Russian oil, in not containing members of the series C_nH_{2n+2}. In this respect, and in respect to the large proportion of aromatic hydrocarbons, California petroleum is unlike any other petroleum that has been examined in this laboratory. Incidentally it may be mentioned that California petroleum differs from other petroleums hitherto examined in the large proportions of oxygen and nitrogen compounds which it contains. These bodies are under investigation in this laboratory.

Study of the portions with high boiling-points, which is now in progress, will have an especial interest, since, when they are separated without decomposition, they form the most valuable constituents of lubricating oils and asphalts that have been separated from petroleum. In some of the high distillates, such as those from Summerland oil, hydrocarbons of the series C_nH_{2n-2} and the series C_nH_{2n-4} have been identified.

XXXVI.—On the Chlorine Derivatives of the Hydrocarbons in California Petroleum.

By Charles F. Mabery and Otto J. Sieplein.

In further confirmation of the composition of the hydrocarbon 68°–70°. described in the previous paper (Mabery and Hudson), the chlorine derivatives were formed by exposing the hydrocarbon over water to the action of chlorine, in ordinary daylight. After washing and drying, the chlorine product was fractioned under atmospheric pressure until it col-

lected at 125° to 130°, and for the most part at 126°. It distilled under normal conditions with the mercury all in the vapor at 125°.5.

The specific gravity at $\frac{20°}{20°}$ was 0.9255; at $\frac{20°}{4°}$, 0.9239; at $\frac{30°}{4°}$, 0.9143; and at $\frac{40°}{4°}$, 0.9044. The coefficient of expansion calculated from the average of these determinations is 0.000918.

A chlorine determination gave the following percentage: 0.1572 gram of the oil gave 0.1872 grams AgCl.

	Calculated for $C_6H_{11}Cl$.	Found.
Cl	29.92	29.50

The molecular weight was determined at the freezing-point of benzene.

1.1641 grams of the oil and 0.1992 gram benzene gave a depression of 2°.482.

Calculated for $C_6H_{11}Cl$.	Found.
118.5	118

The index of refraction at 20° was found to be 1.416, and the molecular refraction 33.29. Required for $C_6H_{11}Cl$, 32.54. Hexamethylene is, therefore, the principal hydrocarbon with this boiling-point.

In distilling the portions of California petroleum below 100°, it has always been observed that a distillate collected at 90° to 91°. To ascertain whether a hydrocarbon were really present with this boiling-point, distillation of the fractions 85°–100° was continued through a tall Hempel column until a larger portion collected at 89° to 90°. The specific gravity of this fraction without purification was 0.7295, $\frac{20°}{20°}$. After thorough treatment, first with common sulphuric acid and then with fuming acid, the specific gravity was not changed (0.7295). The index of refraction of this hydrocarbon at 20° was 1.411, and the molecular refraction 33.35; calculated for C_7H_{14}, 32.22. The molecular weight at the freezing-point was found to be as follows:

0.8669 gram of the oil and 17.62 grams of benzene gave a depression of 2°.547.

Calculated for C_7H_{14}.	Found.
98	99

With the mercury column all in the vapor, bar. 745.3 mm., this hydrocarbon distilled completely at 90°.4.

The chlorine derivative of this hydrocarbon was formed by the action of chlorine over water. After washing, drying, and distillation under atmospheric pressure, the chloride came together at 145° to 150°, for the most part at 147°.

A determination of chlorine gave a value required for the monochloride:

0.1605 gram of the oil gave 0.1696 gram AgCl.

	Calculated for $C_7H_{13}Cl$.	Found.
Cl	26.77	26.13

The specific gravity of the chloride at $\frac{20°}{4°}$ was 0.9332; at $\frac{30°}{4°}$, 0.9316; at $\frac{80°}{4°}$, 0.9231; at $\frac{40°}{4°}$, 0.9138. The coefficient of expansion for 1° calculated from these results is 0.000973.

A determination of the molecular weight at the freezing-point gave the following value:

0.9318 gram of the oil and 19.98 grams of benzene gave a depression of 1°.744.

Calculated for $C_7H_{13}Cl$.	Found.
132.5	131

The index of refraction at 20° was found to be 1.441, and the molecular refraction, 37.57; calculated for $C_7H_{13}Cl$, 37.11.

These results are sufficient to establish the formula for this hydrocarbon as C_7H_{14}. It is probably dimethylpentamethylene. It differs in its properties from methylhexamethylene, boiling-point 99° to 100°: its chloride boils at 147°, while methylhexamethylene chloride boils at 141° to 142°.

Methylhexamethylene Chloride, $C_7H_{13}Cl$.

To ascertain the correct boiling-point of heptamethylene, the distillates 95°–100° were carried through a series of distillations until the greater portion collected at 98° to 100°, and this product distilled for the most part at 99° to 100°, bar. 745°.3, with the mercury column wholly in the vapor.

The empirical formula of this hydrocarbon has been ascer-

tained in the distillates from various specimens of California oils, by analysis and determinations of molecular weight. The boiling-point of hexahydrotoluene, prepared by the addition of hydrogen to toluene, was given as 97°. Markownikoff found that the same hydrocarbon separated from Russian petroleum, and also the synthetically prepared heptanaphthene, boiled at 101°.

For further identification of our product it seemed advisable to study its derivatives. The chlorine derivative was first formed by passing chlorine into the hydrocarbon over water until the greater part was converted into the chloride. This reaction takes place very readily in ordinary daylight, and with a large generator the action of chlorine may be made continuous, saving much time in the chlorination. This method seems to be more advantageous than that formerly used by us in which dry chlorine was allowed to act on the vapor of the dry oil. The chlorinated oil was washed, dried over calcium chloride, and fractioned. After five distillations through a Hempel column, a considerable portion collected at 141° to 142°, which proved to be the monochloride, and more remained above 160°, which was doubtless the dichloride.

A determination of chlorine in the fraction 141°–142°, by the method of Carius, gave a value required for $C_7H_{13}Cl$:

0.1863 gram of the oil gave 0.2025 gram AgCl.

	Calculated for $C_7H_{13}Cl$.	Found.
Cl	26.77	26.88

The molecular weight was also determined by the Beckmann freezing-point method:

1.1960 grams of the oil and 25.8960 grams benzene gave a depression of 1°.701.

Calculated for $C_7H_{13}Cl$.	Found.
132.5	133

The specific gravity of the monochloride at 20° was found to be 0.9310. For further confirmation of the formula, the index of refraction was determined with the aid of a Pulfrich refractometer, and from the density and molecular weight the

molecular refraction was calculated. The index of refraction found was 1.441, and the molecular refraction:

Calculated for $C_7H_{13}Cl$.	Found.
37.11	37.57

The theoretical value was calculated on the assumption that all the carbon atoms are singly connected.

In order to ascertain whether the chlorine atom enters the ring or side chain, the nitril was formed by heating the chloride with alcoholic potassic cyanide for several hours. There was an abundant separation of potassic chloride, and on diluting the solution the nitril separated as an oily liquid above the water. This oil had the characteristic odor of the nitrils. Its specific gravity at 20° was 0.9253, and its index of refraction 1.45. The molecular refraction, assuming the molecular weight, was 35.78, calculated from the elements, assigning to the cyanogen group the value 5.33, which was determined from ethyl cyanide, C_2H_5CN. The theoretical molecular refraction for the nitril calculated on the same basis is 36.45.

The nitril was saponified by heating it to 110° with concentrated hydrochloric acid. The acid formed had the odor of alphatoluic acid, but the amount obtained was not sufficient for complete examination.

When heptamethylene chloride was brought together with metallic sodium, a vigorous action soon set in with the evolution of great heat, sufficient to cause the decomposition of the products unless it was controlled by cooling. This reaction was best carried on by dissolving the chloride in ether, adding the sodium in slight excess over the calculated amount, and keeping the solution cold. In two hours the reaction was complete. The products included an unsaturated hydrocarbon, boiling-point 97°, and another hydrocarbon, boiling-point approximately 220° to 230°. That the hydrocarbon boiling at 97° was unsaturated was shown by the formation of a bromine addition-product; bromine was added readily in the cold with no escape of hydrobromic acid. A Carius determination of the bromine in this product gave the following result:

0.2045 gram of the oil gave 0.3023 gram AgBr.

	Calculated for $C_7H_{13}Br_3$.	Found.
Br	62.5	62.9

The specific gravity of the dibrom derivative at 20° was 1.648. A determination of its molecular weight was made:

0.9238 gram of the oil and 25.3 grams of benzene gave a depression of 0°.725.

Calculated for $C_7H_{13}Br_3$.	Found.
256	247

The odor of the unsaturated hydrocarbon was very sharp and penetrating, very different from that of the paraffin and methylene hydrocarbon, but resembling the olefines. In further proof that it contained doubly bonded carbon, it was titrated with the Hübl reagent, an alcoholic solution of iodine and mercuric chloride. The amount of iodine absorbed was approximately equivalent to two atoms of iodine for each molecule of the hydrocarbon. When heated with hydriodic acid, the monoiodide was readily formed. The specific gravity of the unsaturated hydrocarbon at 20° was 0.7472. Its molecular weight was ascertained by the freezing-point method:

0.7116 gram of the oil and 25.19 grams of benzene gave a depression of 1°.420.

Calculated for C_7H_{13}.	Found.
96	98

The index of refraction of sodium light was found to be 1.416. The molecular refraction calculated from the density and molecular weight was:

$C_6H_5CH_3$.	Calculated for $C_6H_{10}{=}CH_2$.	Found.
30.06	31.77	32.34

These values indicate that the unsaturated hydrocarbon contains a double bond between the side-chain carbon and a carbon atom in the ring, confirming the position of the chlorine atom in the side chain, which is indicated by the ease with which it is replaced in the reaction with potassic cyanide. The form that the chlorination takes doubtless depends on the fact that the hydrogen in the side chain is less firmly bound

than the hydrogen atoms in the methylene ring. The unsaturated condition $C_6H_{10}=CH_2$ is shown by the action of halogens and haloid acids, and confirmed by the molecular refraction, which corresponds to the sum of the atomic refractions assuming the double bond.

This constituent of California petroleum is therefore identical with methylhexamethylene, which may be formed by the addition of hydrogen to toluene.

The hydrocarbon with a boiling-point 220° to 230°, formed by the action of sodium on methylhexamethylene chloride, doubtless contains two methylene rings:

$$C_6H_{11}CH_2—CH_2C_6H_{11}.$$

The quantity of this product formed was too small for identification, but it evidently affords a means for building up the higher methylene hydrocarbons containing more than one methylene ring. That it was a condensed hydrocarbon was shown by its high specific gravity, 0.8872.

Dimethylhexamethylene Chloride, $C_8H_{15}Cl$.

The formula of dimethylhexamethylene was ascertained, as shown in the previous paper, by analysis and determination of its molecular weight. The formula was still further verified by the formation of the chlorine derivative. As in the chlorination of methylhexamethylene, chlorine was allowed to act on the hydrocarbon over water in ordinary daylight until it was nearly all converted into the chlorine derivative. After washing and drying, the product was distilled under atmospheric pressure; after several distillations the monochloride collected in larger part at 168° to 170°. The specific gravity of this product at 20° was found to be 0.9358. A determination of chlorine gave the following result:

0.2034 gram of the oil gave 0.1973 gram AgCl.

	Calculated for $C_8H_{15}Cl$.	Found.
Cl	24.21	24.01

The molecular weight of the chloride was determined by the freezing-point method:

0.7293 gram of the oil and 25.66 grams benzene gave a depression of 0°.982.

Calculated for $C_8H_{15}Cl$.	Found.
146.5	142

The index of refraction for sodium light at 20° was 1.455, and the molecular refraction:

Calculated for $C_8H_{15}Cl$.	Found.
41.69	41.60

That the chlorine enters a side chain in this reaction, as in the case of methylhexamethylene, appears from the ready formation of the nitril by heating the chloride with alcoholic potassic cyanide. On diluting the solution the nitril separated as an oil, with the characteristic odor of the nitrils. It was saponified by heating with aqueous potassic hydrate. On acidifying the solution, a solid was precipitated with an odor characteristic of the α-toluic acids, but the quantity obtained was not sufficient for identification. It was probably meta-methyl-α-toluic acid.

Trimethylhexamethylene Chloride, $C_9H_{17}Cl$.

This chloride was also formed, washed, dried, and fractioned under atmospheric pressure. It came together in larger quantity at 186°–188°; its specific gravity at 20° was 0.9380. The percentage of chlorine was determined.

0.2300 gram of the oil gave 0.2041 gram AgCl.

	Calculated for $C_9H_{17}Cl$.	Found.
Cl	22.10	21.94

The molecular weight was also ascertained at the freezing-point:

0.8672 gram of the oil and 25.03 grams benzene gave a depression of 1°.090.

Calculated for $C_9H_{17}Cl$.	Found.
160.5	156

In further support of the formula of the chloride, the index of refraction was determined, 1.462, and the molecular refraction calculated.

Calculated for $C_9H_{17}Cl$.	Found.
46.3	47

When sodium was allowed to act on trimethylhexamethylene chloride, a vigorous reaction set in that could be controlled by cooling. By carrying on the reaction in an ethereal solution on standing over night in water the reaction was complete. The product of the reaction consisted for the most part of an unsaturated hydrocarbon, and a smaller quantity of a heavy oil, doubtless formed by the union of two methylene rings. The boiling-point of the unsaturated hydrocarbon was 135° to 140°. Its unsaturated condition was shown by the readiness with which it united with iodine in Hübl's reagent, absorbing approximately 2 atoms of iodine. The specific gravity of the unsaturated hydrocarbon at 20° was 0.7762. The molecular weight at the freezing-point was determined.

0.8572 gram of the oil and 22.45 grams benzene gave a depression of 1°.571.

Calculated for C_9H_{18}.	Found.
124	120

The index of refraction was found to be 1.431, and the molecular refraction :

$C_6H_7(CH_3)_3$.	Calculated for $C_6H_5(CH_3)_2{=}CH_2$.	Found.
39.26	40.97	41.46

Dekanaphthene Chloride, $C_{10}H_{19}Cl$.

In confirmation of the formula of dekanaphthene, the index of refraction was determined and the molecular refraction calculated. The density 0.7898, the index 1.4325, and the molecular weight gave the following value :

Calculated for $C_{10}H_{20}$.	Found.
46.10	46.00

The chlorine derivative of this hydrocarbon was formed by passing in chlorine over water. After washing, drying, and fractioning *in vacuo*, the chloride collected in larger quantities at 105° to 110° (50 mm.). Another portion collected at 140° to 145°, probably a dichloride. The specific gravity of the monochloride at 20° was 0.9470. A determination of chlorine gave the following value :

0.1840 gram of the oil gave 0.1476 gram AgCl.

	Calculated for $C_{10}H_{19}Cl$.	Found.
Cl	20.33	19.80

The molecular weight of the chloride at the freezing-point of benzene was also determined :

1.2536 grams of the oil and 21.29 grams benzene gave a depression of 1°.689.

Calculated for $C_{10}H_{19}Cl$.	Found.
174.5	171

A determination of the index of refraction of this chloride gave 1.468. The molecular refraction was calculated as follows :

Calculated for $C_{10}H_{19}Cl$.	Found.
50.89	51.34

On account of the small quantity of the dichloride obtained, it was not possible to purify it completely by distillation. But a determination of chlorine gave 31.53 per cent ; required for $C_{10}H_{18}Cl_2$, 33.90. A determination of molecular weight gave 199 ; required for the dichloride, 209. The molecular refraction calculated from the index was 56.98 ; calculated from the formula, 55.81. On account of the differences between the theoretical values for the mono- and dichlorides, these values are sufficient to show that the dichloride was formed and separated in nearly a pure form.

Undekanaphthene Chloride, $C_{11}H_{21}Cl$.

The index of refraction of this hydrocarbon was found to be 1.4403, and the molecular refraction :

Calculated for $C_{11}H_{22}$.	Found.
50.70	50.63

This determination was made in the distillate 190°–192°, which was used for all work on this hydrocarbon.

The chlorine derivative was prepared in the same manner as those of the hydrocarbons previously described. On fractioning it *in vacuo* at 35 mm. it collected for the most part at 125° to 130°. Its specific gravity was found to be 0.9583 at 20°. A chlorine determination supported the formula of the monochloride.

0.1560 gram of the oil gave 0.1179 gram AgCl.

	Calculated for $C_{11}H_{21}Cl$.	Found.
	18.81	18.69

The molecular weight was determined at the freezing-point of benzene.

0.6055 gram of the oil and 17.37 grams benzene gave a depression of 0°.890.

Calculated for $C_{11}H_{21}Cl$.	Found.
188.5	192

The index of refraction was found to be 1.476, and the molecular refraction:

Calculated for $C_{11}H_{21}Cl$.	Found.
55.48	54.32

The composition of its chloride, together with its molecular weight and molecular refraction, all show that the boiling-point of undecane is 194° to 196°.

Dodekanaphthene Chloride, $C_{12}H_{23}Cl$.

The index of refraction of dodekanaphthene was found to be 1.4649, and the molecular refraction:

Calculated for $C_{12}H_{24}$.	Found.
55.38	55.24

The chlorine derivative was formed, washed, dried, and fractioned *in vacuo*. It collected for the most part at 130°–135° (17 mm.). Its specific gravity at 20° was 0.9616. A determination of chlorine gave the following result:

0.1657 gram of the oil gave 0.1153 gram AgCl.

	Calculated for $C_{12}H_{23}Cl$.	Found.
Cl	17.52	17.20

The molecular weight was also determined:

0.7172 gram of the oil and 19.04 grams benzene gave a depression of 0°.925.

Calculated for $C_{12}H_{23}Cl$.	Found.
202.5	204

The index of refraction was 1.480, and the molecular refraction:

Calculated for $C_{13}H_{23}Cl$.	Found.
60.77	59.96

Tridekanaphthene Chloride, $C_{13}H_{25}Cl$.

The index of refraction of this hydrocarbon as determined is 1.4745, and its molecular refraction:

Calculated for $C_{13}H_{26}$.	Found.
60.25	59.84

The chlorine derivative was formed by the action of chlorine, dried and fractioned under 17 mm.; it came together for the most part at 140° to 145°. Its specific gravity at 20° was 0.9747; a Carius determination gave the following percentage of chlorine:

0.1674 gram of the oil gave 0.1137 gram AgCl.

Calculated for $C_{13}H_{25}Cl$.	Found.
16.38	16.78

In the chlorine derivatives of the higher hydrocarbons the weight of the oil that can be taken for analysis is limited, since as in the last analysis the pressure of the large volume of gases formed is more than the tube can stand. The molecular weight of tridekanaphthene chloride was determined at the freezing-point of benzene:

0.4447 gram of the oil and 17.88 grams benzene gave a depression of 0°.763.

Calculated for $C_{13}H_{25}Cl$.	Found.
216.5	217

Tetradekanaphthene Chloride, $C_{14}H_{27}Cl$.

Tetradekanaphthene chloride was readily formed by passing chlorine into the hydrocarbon over water in ordinary daylight; if the action was stopped with a small portion of the hydrocarbon unacted on, the product consisted for the larger part of the monochloride. After washing and drying, the chlorine derivative was separated by continued distillation *in*

vacuo under 13 mm.; it came together for the most part at 150° to 155°. The specific gravity of the monochloride was 0.9748, $\frac{20°}{20°}$; at $\frac{20°}{4°}$, 0.9730; at $\frac{30°}{4°}$, 0.9661; and at $\frac{40°}{4°}$, 0.9579. The mean coefficient of expansion, within 20° to 40°, from these results, is 0.00078.

A determination of chlorine gave a value required for the monochloride:

0.1559 gram of the oil gave 0.0989 gram AgCl.

	Calculated for $C_{14}H_{27}Cl$.	Found.
Cl	15.39	15.80

As mentioned above, the decreasing proportion of chlorine in these derivatives with the increasing molecular weight, and the consequent larger volumes of gases, beyond the strength of the ordinary Carius tubes, gives a smaller weight of silver chloride than could be desired, but the accuracy of the method permits of sufficiently reliable results, even with the small weights.

The molecular weight of the chloride was determined at the freezing-point of benzene:

0.8923 gram of the oil and 17.76 grams benzene gave a depression of 1°.094.

Calculated for $C_{14}H_{27}Cl$.	Found.
230.5	225

The index of refraction was found to be 1.493, and the molecular reaction 68.67; calculated for $C_{14}H_{27}Cl$, 69.37.

The boiling-point of this chloride cannot be accurately determined under atmospheric pressure because it is rapidly decomposed at the higher temperature and in presence of air, although it may be distilled indefinitely *in vacuo*. Probably the boiling-point under atmospheric pressure is not far from 275°.

Pentadekanaphthene Chloride, $C_{15}H_{29}Cl$.

This chloride was prepared from pentadekanaphthene which had been well fractioned *in vacuo*. These higher chlorides are formed as readily as the lower ones. After washing and fractional distillation under 14 mm. this monochloride came to-

gether for the most part at 170° to 175° without decomposition. Its boiling-point under atmospheric pressure is probably near 300°. Its specific gravity at $\frac{20°}{4°}$ was 0.9771; at $\frac{20°}{4°}$, 0.9753; at $\frac{18°}{4°}$, 0.9714; and at $\frac{4°}{4°}$, 0.9643. The coefficient of expansion calculated from these values is 0.000576. A Carius determination gave the required percentage of chlorine.

0.1536 gram of the oil gave 0.0923 gram silver chloride.

Calculated for $C_{15}H_{29}Cl$.	Found.
14.51	14.85

A determination of the molecular weight supported the same formula.

0.9073 gram of the oil and 18.93 grams benzene gave a depression of 0°.984.

Calculated for $C_{15}H_{29}Cl$.	Found.
244.5	239

The index of refraction was 1.493, and the molecular refraction 72.90; calculated for $C_{15}H_{29}Cl$, 73.97.

Attempts will be made to form the chlorides of the higher hydrocarbons in connection with the study of the composition of these bodies.

XXXVII.—On the Composition of Japanese Petroleum.

By Charles F. Mabery and Shinichi Takano.[1]

The oil fields in Japan are the most promising and are under the most rapid development of any recently discovered oil territory. The output in 1891 was 56,000 bbls. annually; in 1899 it was 1,000,000 bbls. The oil territory in Japan is contained in the province of Echigo, at least to the extent of 90

[1] Mr. Takano has spent three years in the study of petroleum in this country, having been sent for this purpose by the Japanese government. He is thoroughly familiar with the geology of the oil territory in Japan, having given especial attention to this subject in a thesis which he presented for a degree in the University of Tokio. Besides a thorough knowledge of the composition of petroleum from a chemical point of view, which he has gained during the two years he has spent exclusively in the study of this subject in this laboratory, Mr. Takano spent one year as a laborer in different refineries, where he took charge by actual manipulation of every process in the preparation of commercial products. The work presented in this paper formed the subject of a thesis by Mr. Takano for the degree of M.S.

per cent on the northern coast of the Sea of Japan. This province is surrounded in part by a mountain chain which encloses a section of country 140 miles long by 150 miles broad, rising gradually from the sea to the mountains with a varying altitude from 150 to 500 feet. Oil is found chiefly in the Upper Eocene of the Tertiary formation, where it is held under pressure between impervious layers of slate and sandstone.

Nodules of calcite are frequently found embedded in the sandstone, and crystals of calcite twinned, resembling those found in the Ohio Trenton-limestone, oil-bearing rock. The oil strata are full of sea shells, a good indication as to the origin of the oil formations. There are great variations in the depths of the wells. For example, the wells of the Amaze field are approximately 2,000 feet in depth, while those of the Miyagawa field, only 6 miles distant, are 700 feet deep. The wells of the Niitsu field are still shallower, 600 feet. The Nagaoka wells are 800 feet in depth. Nevertheless, the oil strata at the different depths are essentially of the same formation. The sandstone in which the Nagaoka oil is found is coarser than that of the other fields. On the surface of the Niitsu oil territory are immense beds of peat which are used for fuel.

Although the oil fields of Japan are situated in close proximity, specimens of oil from the different fields differ as essentially in composition as the variations in specific gravity indicate. As will appear later, the Amaze, Miyagawa, and Hirei fields yield paraffin in considerable quantities. While the hydrocarbons above C_7H_{14} do not include members of the series C_nH_{2n+2}, at least so far as it appears from analysis of distillates prepared on a laboratory scale, the lower distillates do contain members of the paraffin series.

The paraffin hydrocarbons with low boiling-points, such as the butanes, pentanes, and hexanes, have an agreeable sweetish odor that is easily recognizable, and quite different from the pungent harsh odor of the methylenes. The odor of the paraffins is more apparent in the Miyagawa oil than in any other of the Japanese oils we have seen, and somewhat less in the Amaze oil. When these hydrocarbons with low boiling-points are present, the crystalline paraffin hydrocarbons C_nH_{2n+2} are usually to be found.

Considerable quantities of gas were formerly obtained from the Amaze oil territory, but the supply now seems to be exhausted, at least so far as wells have been bored; some gas escapes from the shallow Miyagawa wells, more from the shallow wells of the Niitsu territory. As wells are sunk deeper in this territory it is probable that lighter oils will be found. On account of the friable condition of the oil rock and the danger of clogging the wells by loose material, "shooting" the wells after boring is not practiced. The flow from the wells is irregular; frequently it will amount to 300 barrels a day for a week, and then stop, and the oil must be pumped.

The oil territory in Japan includes the following fields: Amaze, Nagaoka, Niitsu, and Hiyama. The different sections of the oil territory may be classified as follows:

Amaze	Amaze, Miyagawa, Gendogi	green oil
Nagaoka	Hirei, Kitatani, Katsudo	dark oil
Niitsu	Koguchi, Kusodsu	
Hiyama	Hiyama	dark green oil.

The Amaze field is the oldest; the Hiyama field has been most recently developed; both these oils contain paraffin.

The crude oils from the different fields differ essentially in their properties, as shown by the different specific gravity, the different percentages of sulphur, nitrogen, and the differ-

	Amaze.	Hirei.	Katsudo.	Kitatani.
Specific gravity	0.8245	0.8622	0.8771	0.8952
Per cent sulphur	0.23	0.41	0.82	0.61
" nitrogen	0.35	0.74	0.97	0.75
Iodine absorption	0.0	0.84	7.66	0.82
Coefficient of expansion	82.5	78.5	76.5	79.5

	Koguchi.	Kusodsu.	Miyagawa.
Specific gravity	0.9435	0.9210	0.8911
Per cent sulphur	0.49	0.37	0.32
" nitrogen	1.34	1.23	0.55
Iodine absorption	9.79	0.62	1.63
Coefficient of expansion	67.5	61.5	74.5

Percentages of Distillates.

	Amaze.	Hirei.	Katsudo.	Kitatani.	Koguchi.	Kusodsu.	Miyagawa.
—150°	22.8	21.8	22.2	14.0	0.0	0.0	15.0
150°–300°	40.2	38.3	38.8	38.8	25.0	25.0	36.8
+300°	37.0	39.9	39.0	47.2	75.0	75.0	48.2

ent proportions in which they distil at different temperatures. There are also marked differences in iodine absorption, and in the coefficients of expansion. The latter were determined by ascertaining the specific gravity at 5°, 10°, 20°, and 25°, and dividing the differences in specific gravity at the different temperatures by 5 and multiplying the quotient by 100,000, the method described in Redwood's treatise on petroleum.

In the development of oil territory hitherto, no attempts have been made to ascertain the series of hydrocarbons which compose the main body of the crude oil. Beside the work of Pelouze and Cahours, Schorlemmer, and Warren on the Pennsylvania and Canadian oils, and the work carried on in this laboratory, no attempts have been made to determine the form of the hydrocarbons in the lower distillates of American oils, and nothing whatever beside the unpublished work of this laboratory on the determination of the composition of the portions with higher boiling-points. Beside the work of Markownikoff on the Russian oils and the work of Warren and Storer on Rangoon petroleum, very little has been done in this direction on oils from other fields. On account of the ease in the preparation of commercial products from the lighter oils of Pennsylvania and Ohio, the ultimate composition was of less importance than it is now becoming in the development of oil fields that yield heavier crude oils, such as the oil territory in California, Texas, South America, Japan, and numerous other fields recently discovered. The methods that must be applied to these heavy oils are essentially different from the methods that have been universally in use since the beginning of the oil industry. In Japan, the promoters of those oil fields will have the advantage not only of all former experience in oil refining, but the further advantage of a knowledge of the hydrocarbons which form the main body of the crude oils. Japanese petroleum apparently differs from other heavy petroleums in that it contains smaller amounts of

the homologues of benzene. Benzene and its homologues were found in the Amaze oil, and some of the other crude oils, but fuming sulphuric acid failed to reduce materially the specific gravity of several of the distillates that should yield benzene hydrocarbons, if they were present.

Constituents of Petroleum from the Amaze Field.

The lightest oil from the Japanese fields is found in the Amaze territory. It consequently contains the largest proportion of more volatile constituents. A combustion of Amaze crude oil gave 84.66 per cent carbon and 13.22 per cent hydrogen. After several distillations under a Hempel column, fractions collected in larger quantities at 68°, 98°, 119°, 135°, 162°, 196°, 216°. No attempts were made to ascertain the form of the hydrocarbons below 68°. The distillate collected at 68° had the specific gravity 0.7343, which indicated that hexane was not present in any considerable quantity; but nothing further was done toward identifying hexamethylene, which no doubt is the principal hydrocarbon in this distillate.

The distillate collected at 98° to 100°, after purifying with fuming sulphuric acid, gave as its specific gravity, at 20°, 0.7450.

A combustion gave the following percentages of carbon and hydrogen:

0.1347 gram of the oil gave 0.4221 gram CO_2 and 0.1721 gram H_2O.

	Calculated for C_7H_{12}.	Found.
C	85.70	85.45
H	14.30	14.20

Its index of refraction was found to be 1.4174, and the molecular refraction, 33.14; calculated for C_7H_{14}, 32.22. This hydrocarbon was therefore methylhexamethylene.

The distillate 118°–120°, after purification with fuming sulphuric acid, gave 0.7621 as its specific gravity at 20°. A combustion gave the following percentages of carbon and hydrogen:

0.1406 gram of the oil gave 0.4378 gram CO_2 and 0.1812 gram H_2O.

	Calculated for C_8H_{16}.	Found.
C	84.70	84.94
H	14.30	14.33

A determination of the index of refraction of this oil gave 1.4256, and the molecular refraction 37.68; calculated for C_8H_{16}, 36.82. This hydrocarbon was therefore dimethylhexamethylene.

The distillate collected at 134° to 135°, was purified with fuming sulphuric acid and analyzed.

0.1528 gram of the oil gave 0.4805 gram CO_2; and 0.1950 gram H_2O.

	Calculated for C_9H_{18}.	Found.
C	85.70	85.76
H	14.30	14.29

Its specific gravity, at 20°, was 0.7787.

The refractive index of this oil was found to be 1.4348, and the molecular refraction 42.27; calculated for C_9H_{18}, 41.42. This constituent was therefore trimethylhexamethylene.

A distillate collected in considerable quantity at 160° to 162°, which was purified with fuming sulphuric acid and analyzed:

0.2055 gram of the oil gave 0.6445 gram CO_2; and 0.2556 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.50
H	14.30	13.82

This oil had the specific gravity, 0.7902, at 20°. Its index of refraction was 1.4418, and its molecular refraction 46.94; calculated for $C_{10}H_{20}$, 46.03.

The distillate at 190° to 192°, after purification with fuming sulphuric acid, had the specific gravity, 0.8061, at 20°. Its composition was determined by analysis:

0.1612 gram of the oil gave 0.5046 gram CO_2; and 0.2025 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	85.35
H	14.30	13.96

The molecular weight of this hydrocarbon at the freezing-point of benzene was 166; calculated for $C_{11}H_{22}$, 154. The index of refraction at 20° was 1.4482, and the molecular refraction 51.24; calculated for $C_{11}H_{22}$, 50.63.

The distillate 212°–214°, purified with fuming sulphuric acid, had the specific gravity, 0.8165, at 20°. A combustion gave the following proportions of carbon and hydrogen:

0.1875 gram of the oil gave 0.5879 gram CO_2 and 0.2451 gram H_2O.

	Calculated for $C_{13}H_{24}$.	Found.
C	85.70	85.51
H	14.30	14.52

A determination of its molecular weight at the freezing-point gave 172; calculated for $C_{13}H_{24}$, 168. Its index of refraction was 1.4535, and the molecular refraction 55.76; calculated for $C_{13}H_{24}$, 55.23.

Composition of the Portions of Japanese Petroleum with High Boiling-points.

Japanese petroleum from different sources differs materially in its composition. From such oils as the Hirei no crystalline solids can be separated even at low temperatures. But from others, such as the Amaze, Miyagawa, and Hiyama, crystalline solids separate from the higher fractions. The fraction 310°–315° atmospheric pressure, from Amaze crude oil became solid on cooling. The solid portion was separated by cooling and filtration; it was washed, pressed, and warmed with gasoline, which removed all color. Melting-point, 68°. The fractions between 225° were collected *in vacuo* under 30 mm. The purified solid from 225° to 230° melted at 70°, that from 250° to 275° at 73°, and that from 260° to 265° at 74°. The solid from 225° to 230° gave, by combustion, values showing it to belong to the series C_nH_{2n+2}.

0.1535 gram of the oil gave 0.4890 gram CO_2 and 0.1787 gram H_2O.

	Calculated for $C_{13}H_{24}$.	C_nH_{2n}.	Found.
C	85.14	85.70	85.29
H	14.86	14.30	14.99

The fraction 250°–260°, 30 mm., from the Amaze oil, gave the following percentages by combustion, also showing the series C_nH_{2n+2}:

0.1654 gram of the oil gave 0.5161 gram CO_2; and 0.2233 gram H_2O.

C	85.03
H	15.00

A combustion of the fraction 265°–270° gave values required for a hydrocarbon of the series C_nH_{2n+2}:

0.1750 gram of the oil gave 0.5469 gram CO_2; and 0.2346 gram H_2O.

C	85.21
H	14.81

In determining the molecular weight of this hydrocarbon at the boiling-point of benzene, the following result was obtained:

0.4190 gram of the oil and 24.3 grams benzene gave a rise in boiling-point of 0.126.

Calculated for $C_{26}H_{54}$.	Found.
367	367

Determinations by the boiling-point method of hydrocarbons with such high molecular weights are of necessity somewhat uncertain on account of the slight rise in boiling-point. The question of the molecular weights of these solid hydrocarbons will receive more attention with the constituents of Pennsylvania and California petroleums with high boiling-points.

The specific gravity of the solid 250°–260° is nearly the same as that of the corresponding hydrocarbon from Pennsylvania petroleum:

	Japanese. 250°–260°, 30 mm.	Pennsylvania,[1] 292°–295°, 50 mm.
60		0.7977
70	0.7943	0.7950
80	0.7920	0.7943
90	0.7918	

[1] Unpublished data.

The specific gravity of the Japanese solid at 60° could not be determined, because it was not liquid at that temperature.

Miyagawa Petroleum.

Although this oil is from a field situated only six miles from the Amaze field, it differs essentially in its specific gravity, and in the proportions in which it distils, from the Amaze oil. The crude oil was distilled under atmospheric pressure, and the distillation of the lower portions continued until they came together in larger quantities at temperatures at which distillates were collected from the other oils. The specific gravity of the distillates, after treating with concentrated sulphuric acid, is as follows:

98°–100°.	118°–120°.	134°–136°.	160°–162°.	194°–196°.	212°–214°.	228°–130°.
0.7364	0.7631	0.7772	0.8088	0.8493	0.8674	0.8770

The last three fractions were also treated with fuming sulphuric acid and the specific gravity determined;

194°–196°.	212°–214°.	228°–230°.
0.8412	0.8650	0.8720

The slight change after the thorough treatment with fuming sulphuric acid shows that no homologues of benzene were present in these portions, yet the specific gravity of the hydrocarbons above 196° is considerably higher than of those from Amaze oil or from Hirei oil. The distillates collected under atmospheric pressure were thoroughly treated with fuming sulphuric acid, washed, dried, and their molecular refraction determined:

Distillate.	Refractive index.	Molecular refraction. Calculated.	Required.
98°–100°	1.4117	33.14	32.21
118°–120°	1.4163	36.92	36.82
134°–136°	1.4261	41.51	41.42
160°–162°	1.4463	46.26	46.03
194°–196°	1.4605	50.27	50.63
214°–216°	1.4706	54.34	55.23

Hirei Petroleum.

A combustion of Hirei crude oil gave 82.28 per cent of carbon and 13.19 per cent of hydrogen. In the distillation of the Hirei oil, fractions collected within the same limits of temper-

ature as those from the other crude oils. The distillate collecting in the vicinity of 98°, after treatment with sulphuric acid, gave 0.7412 as its specific gravity. Its molecular weight at the freezing-point of benzene was 98; required for C_7H_{14}, 98. Its index of refraction was 1.4095, and its molecular refraction, 32.77; required for C_7H_{14}, 32.22.

The fraction 118°–120° had the specific gravity 0.7523. Its molecular weight was 114; required for C_8H_{16}, 112. Its index of refraction was 1.4151, and its molecular refraction 37.34; required for C_8H_{16}, 36.82.

The fraction at 135° had the specific gravity 0.7676. Its molecular weight was 128; required for C_9H_{18}, 126. Its index of refraction was 1.4372, and its molecular refraction 42.12; required for C_9H_{18}, 41.42.

The fraction 162° had the specific gravity 0.7887. Its molecular weight was found to be 137; required for $C_{10}H_{20}$, 140. Its index of refraction was 1.4372, and its molecular refraction 46.60; required for $C_{10}H_{20}$, 46.03.

The specific gravity of the fraction at 196° was 0.8192. Its index of refraction was 1.4516, and its molecular refraction 50.78; required for $C_{11}H_{22}$, 50.63.

The specific gravity of the fraction 216° was 0.8327, and the molecular weight 172; required for $C_{12}H_{24}$, 168. Its index of refraction was 1.4599, and its molecular refraction, 55.22; required for $C_{12}H_{24}$, 55.23.

The specific gravity of these distillates from Hirei oil is somewhat higher than was found in the corresponding distillates from Amaze oil, and the differences increase with increasing molecular weights. It was at first thought that this was due to incomplete removal of benzene hydrocarbons, but still further treatment with fuming sulphuric acid failed to diminish these values. It is probable that the oil contains hydrocarbons with more than one methylene ring.

The results of this examination show that Japanese petroleum is composed for the greater part of hydrocarbons of the series C_nH_{2n},—the methylene hydrocarbons. Probably the very heavy oils contain hydrocarbons with two or more methylene rings, of the series C_nH_{2n-2} or C_nH_{2n-4}. Some of the oils contain solid paraffin hydrocarbons, others do not.

The proportion of benzene derivatives in the oils examined is relatively much smaller than in California petroleum. The proportion of nitrogen compounds and of sulphur compounds is quite variable. In some of the oils the percentages were nearly as large as any found in California petroleum, in others the amounts were much smaller.

THE BASIC NITRATES OF BISMUTH.

By F. B. Allan.

When bismuth nitrate is treated with water, it is decomposed, forming a basic nitrate, $BiONO_3$, which has been described by Duflos,[1] Heintz,[2] Becker,[3] Ditte,[4] and others. It is said to have one, two, or three molecules of water of crystallization, according to the method of preparation.

Numerous other basic nitrates have also been described:

A. $6Bi_2O_3.5N_2O_5 + 9H_2O$.—Bismuth nitrate, or a solution of bismuth in nitric acid, is added to water above 50° (Becker).

B. $5Bi_2O_3.4N_2O_5 + 9H_2O$.—A solution of bismuth nitrate is added to water at 40° to 50°; after twenty-four hours three-quarters of the liquid is poured off and more water at 50° is added; when the liquid has cleared, the precipitate is filtered off and washed with cold water (Becker).

C. $11Bi_2O_3.9N_2O_5 + 21H_2O$.—Same preparation as *B* (Janssen).[5]

D. $4Bi_2O_3.3N_2O_5 + 9H_2O$.—*A* is washed till the wash-water gives no acid reaction (Becker).

E. $5Bi_2O_3.3N_2O_5 + 8H_2O$.—(*a*) The salt $BiONO_3$ is dissolved in a large quantity of water which, after some time, deposits a precipitate without crystalline structure (Becker).

(*b*) The salt $BiONO_3$ is mixed with twenty-four times its weight of water and dilute sodium hydroxide is added till the liquid scarcely reddens litmus (Duflos, Janssen).

F. $2Bi_2O_3.N_2O_5 + H_2O$.—The salt $BiONO_3$ is decomposed by water at 100° (Ditte).

[1] Archiv. der Pharm., [2], **23**, 307; Pharm. Centrbl., 1840.
[2] J. prakt. Chem., **45**, 102.
[3] Archiv. der. Pharm., **55**, 31, 129; Ann. Chem. (Liebig), **68**, 282.
[4] Compt. rend., **79**, 956.
[5] Archiv. der Pharm., 68, 1, 129; Forts. der Chem., 1851.

It will be seen that, in most of the above preparations, no account of the composition of the mother-liquor is given. Ditte has shown that water at 10° will decompose the neutral nitrate, giving the so-called subnitrate ($BiONO_3$), only until it contains 83 grams of nitric anhydride per liter, and that a nitric acid solution stronger than that does not decompose bismuth nitrate. He also found that, at 100°, the change from the form $BiONO_3$ to the form $2Bi_2O_3.N_2O_5$ took place only when the water contained less than 4.5 of grams of nitric anhydride per liter, and that this reaction was reversible, the subnitrate being again formed when more acid was added to the solution.

The directions for preparing some of these basic nitrates were followed, and Table *A* contains a comparison of the products with those analyzed by Becker and Janssen. The bismuth was estimated as oxide by ignition of the basic nitrate, or, if in solution, by boiling with an excess of a solution of sodium carbonate and ignition of the precipitate, or by evaporation of the solution to dryness and ignition of the residue. The nitric acid was determined by boiling for half an hour with an excess of a solution of sodium carbonate, and estimation of the excess after filtering.

Table A.

			Becker.		Janssen.	
	Bi_2O_3.	N_2O_5.	Bi_2O_3.	N_2O_5.	Bi_2O_3.	N_2O_5.
A	79.65	16.81	79.86	15.55		
B, *C*	78.95	15.93	79.6	14.6	80.17	14.0
D	80.16	15.11	79.2	13.8		
E(*b*)	83.14	12.71	84.3	11.8		

This indicates that the composition of the different products is dependent on conditions which have not been described, and that possibly an examination of these conditions would show that some of these basic nitrates are mixtures. Janssen has endeavored to represent them all as consisting of

$$Bi(NO_3)_3 + 5H_2O \text{ and } 5Bi_2O_3.3N_2O_5 + 8H_2O$$

in varying proportions.

Prof. Miller suggested to me the application of the "phase rule" to this problem. In a system containing bismuth oxide, nitric anhydride, and water, five phases would constitute a

nonvariant system, and a liquid, a gas, and three solid phases could exist only at one temperature, one pressure, and one concentration of the liquid for any three given solid phases. If the system consisted of a liquid, a gas, and two solid phases, it would be monovariant, and we might have such a system at different temperatures or with different concentrations of the liquid, but, at any given temperature, the liquid in equilibrium with two given solid phases could not vary in concentration. In a divariant system, one solid phase might be in equilibrium, at constant temperature, with a liquid of varying concentration, or with a liquid of given concentration at different temperatures. A knowledge of the conditions of equilibrium in such a system will enable us to determine whether one or two solid phases are present.

Neutral bismuth nitrate, or a basic nitrate of known composition, was added to water or a solution of nitric acid, and stirred in a water-bath, at constant temperature, till equilibrium was reached. It was found that these reacted more quickly than bismuth oxide and nitric acid. The stirrer was driven by a water motor and had bottles on both sides of a horizontal shaft in such a way that the contents were thrown from one end of the bottle to the other. The acidity of the liquid was determined from time to time, and when this had become constant the bismuth oxide in solution was also determined, and the difference between the bismuth oxide and nitric anhydride used, and the amount of these in solution gave the composition of the solid contents of the bottles.

The bismuth nitrate used was Kahlbaum's preparation, and the basic nitrate used in the first series of experiments was prepared from it by adding the solution in nitric acid to a large volume of cold water and filtering off the precipitate as soon as it had settled to the bottom of the vessel. There seems to be no difficulty about the preparation of this substance, as repeated experiments gave the same product. One specimen which had been dried in the air for a week gave the following results on analysis:

	Calculated for $BiONO_3 + H_2O$.	Found.
Bi	68.37	68.25
NO_3	20.35	20.30

Table B.

Temp., 21°. $\frac{Bi_2O_3}{N_2O_5}$ in $BiONO_3 = 4.31$; in $6Bi_2O_3.5N_2O_5 = 5.17$.

No.	Salt used.	Components used. Bi_2O_3. Grams.	N_2O_5. Grams.	H_2O. cc.	Acidity of liquid. 6 days. N.	13 days. N.	Bi_2O_3 in solution. Grams.	$\frac{Bi_2O_3}{N_2O_5}$ in solid.
1	$BiONO_3$	1.52	0.351	40	0.0293	0.0293	....	5.24
2	"	3.04	0.703	40	0.054	0.054	....	5.15
3	"	4.56	1.054	40	0.085	0.085	....	5.22
4	"	7.59	1.757	40	0.144	0.145	....	5.25
5	"	1.52	0.673	40		0.184	0.08	5.16
6	"	3.04	1.025	40		0.212	0.10	5.15
7	"	4.55	1.376	40		0.244	0.14	5.17
8	"	6.07	1.727	40	0.267	0.277	0.16	5.21
9	"	1.52	0.866	40		0.283	0.17	5.13
10	"	3.04	1.217	40		0.318	0.21	5.25
11	"	4.56	1.568	40	0.312	0.349	0.28	5.09
12	"	6.07	1.92	40	0.328	0.377	0.31	5.00
13	"	7.59	2.27	40	0.347	0.385	0.37	4.91
14	$Bi(NO_3)_3$	1.74	1.21	40.7		0.426	0.45	4.44
15	"	2.35	1.65	40.9		0.582	0.75	4.32
16	"	2.87	2.01	41.1	0.716	0.717	1.04	4.35

It will be seen that the contents of most of the bottles had come to equilibrium, but Nos. 11, 12, and 13 were still changing. Nos. 1 to 10 had solid contents of constant composition in equilibrium with liquids of different concentrations, and these, therefore, contained but one solid phase, $6Bi_2O_3.5N_2O_5$. Nos. 14 to 16 also contained one solid phase, $BiONO_3$. Nos. 11 to 13 contained the salt $BiONO_3$ partially converted into the salt $6Bi_2O_3.5N_2O_5$, but, as equilibrium had not been reached, the liquid phase was not of constant concentration.

A quantity of the salt $6Bi_2O_3.5N_2O_5$ was prepared by stirring the salt $BiONO_3$ with water, care being taken that the mother-liquor was of a concentration found by the previous experiment to be in equilibrium with that compound. This was used in some of the bottles in the next series. A higher temperature was now used in order that more basic nitrates might be obtained, and, also, that equilibrium might be more quickly reached.

Table C.

Temp. 50°. $\frac{Bi_2O_3}{N_2O_5}$ in $2Bi_2O_3.N_2O_5 = 8.63$.

No.	Salt used.	Components used. Bi_2O_3. Grams.	Components used. N_2O_5. Grams.	Components used. H_2O. cc.	Acidity of liquid. 6 days. N.	Acidity of liquid. 13 days. N.	Acidity of liquid. 19 days. N.	Bi_2O_3 in solution. Grams.	$\frac{Bi_2O_3}{N_2O_5}$ in solid.
1	$6Bi_2O_3.5N_2O_5$	1.53	0.295	40.2	0.057	0.056	0.057	....	8.74
2	"	2.30	0.443	40.3	0.080	0.080	0.081	....	8.59
3	"	3.06	0.590	40.4	....	0.109	0.108	....	8.50
4	"	3.83	0.730	40.5	1.36	....	0.135	0.03	8.63
5	"	4.60	0.873	40.6	1.60	0.159	0.159	0.04	8.64
6	"	6.12	1.164	40.9	....	0.217	0.216	0.07	8.76
7	"	7.66	1.451	41.1	....	0.265	0.265	0.11	8.67
8	"	9.20	1.75	41.3	0.275	0.284	0.286	0.13	8.09
9	"	11.49	2.18	41.6	0.270	0.284	0.283	0.13	7.33
10	"	15.32	2.90	42.2	0.235	0.270	0.276	....	....
11	$BiONO_3$	3.79	0.88	40	0.075	0.242	0.251	....	....
12	"	7.59	1.75	40	0.144	0.193	0.286	0.13	6.27
13	"	11.38	2.63	40	0.216	0.217	0.215	0.08	(5.20)
14	"	15.18	3.51	40	....	0.286	0.284	0.13	5.18
15	"	11.38	2.63	25	....	0.350	0.352	0.17	5.20
16	"	15.18	3.51	25	....	0.467	0.466	0.22	5.17

In this series, Nos. 1 to 7 contained one solid phase, $2Bi_2O_3.N_2O_5$, and Nos. 14 to 16 also contained one solid phase, $6Bi_2O_3.5N_2O_5$. Nos. 8, 9, and 12 were a monovariant system and contained varying proportions of the salts $2Bi_2O_3.N_2O_5$ and $6Bi_2O_3.5N_2O_5$ in equilibrium with liquids of the same composition, as we may neglect the possibility of this being the temperature and concentration at which a nonvariant system can exist. In Nos. 10, 11, and 13, at the first analysis, the solid contents had changed from the form $BiONO_3$ to the form $6Bi_2O_3.N_2O_5$, and the reaction seems to have halted there. They were then seeded with the salt $2Bi_2O_3.N_2O_5$ and, at the end of thirteen days, the reaction had proceeded further in Nos. 11 and 12, but in No. 13 further action had not begun in nineteen days. The same result was observed if the experiment was begun with one of the basic nitrates, and a solution of nitric acid instead of water. No reaction took place for days, the length of time before the reaction began depending on the concentration of the nitric acid.

A series of experiments was begun at 75°, but only three measurements were obtained, as all the other bottles broke at that temperature.

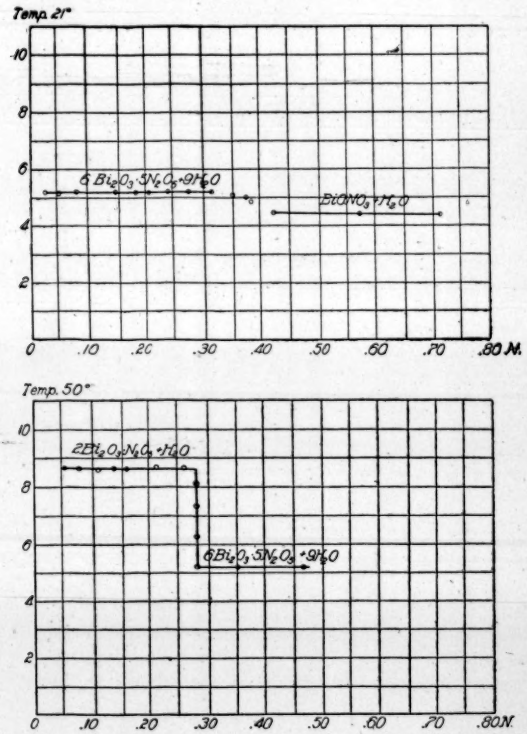
Table D.

Temperature 75°.

No.	Salt used.	Components used. Bi_2O_3. Grams.	Components used. N_2O_5. Grams.	Components used. H_2O. cc.	Acidity of liquid, 2 days. N.	Bi_2O_3 in solution. Grams.	$\frac{Bi_2O_3}{N_2O_5}$ in solid.
1	$6Bi_2O_3.5N_2O_5$	3.06	0.59	40.4	0.109	0.03	8.65
2	"	6.13	1.16	40.9	0.208	0.05	8.68
3	"	9.19	1.75	41.3	0.314	0.15	8.61

If we represent the results given in Tables *B* and *C* in diagrams taking as abscissae the concentration of nitric acid in the liquids in the different bottles expressed in terms of a normal solution, and as ordinates the relation between bismuth oxide and nitric anhydride in the solid contents, horizontal lines represent divariant systems consisting of one solid, a liquid, and a gas, and perpendicular lines represent monovariant systems consisting of two solids, a liquid and a gas. The concentration of the gaseous phase is a function of the concentration of the liquid. In the diagram representing

Table *B* there is no perpendicular line because equilibrium had not been reached in the bottles whose contents are represented between the two horizontal lines.



The solid contents in Nos. 1 to 7, Table *C*, and also those in Nos. 14 to 16 in the same series, were filtered off and dried between filter-paper. An analysis of these two products gave the following results :

	Calculated for $6Bi_2O_3.5N_2O_5 + 9H_2O =$ $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$.	Found.
Bi	71.65	71.70
NO_3	17.77	17.81

	Calculated for $2Bi_2O_3.N_2O_5 + H_2O =$ $Bi_4O_5(NO_3)_2 + H_2O$.	Found.
Bi	78.97	78.86
NO_3	11.76	11.80

Both were impalpable white powders and neither lost in weight when heated for some hours at 100°.

Conclusions.

1. Pouring nitric acid solutions of bismuth into water at ordinary temperature gives only the salt $BiONO_3 + H_2O$ if the precipitate be quickly filtered off, even when the resulting mother-liquor is such as is in equilibrium only with a more basic nitrate. This is due to the fact that where the strong acid solution meets the water and the salt $BiONO_3 + H_2O$ is formed, the concentration of the acid is high, and when the crystalline precipitate comes in contact with the weaker acid the reaction is too slow to produce an appreciable change in a few hours.

2. At 21°, the salt $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$ is in equilibrium with nitric acid solutions from 0.03 to 0.32 normal, and the salt $BiONO_3$ with solutions from 0.425 to 0.72 normal.

3. At 50°, the salt $Bi_4O_5(NO_3)_2 + H_2O$ is in equilibrium with nitric acid solutions from 0.057 to 0.285 normal, and the salt $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$ with solutions from 0.285 to 0.466 normal.

4. At 75°, the salt $Bi_4O_5(NO_3)_2 + H_2O$ is in equilibrium with solutions of nitric acid from 0.109 to 0.314 normal.

5. That no basic nitrate containing a greater proportion of nitric anhydride than the salt $Bi_4O_5(NO_3)_2 + H_2O$ and less than the salt $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$ exists at 50°, although at least two were said to have been prepared at that temperature.

6. That the slowness of the reaction, or a concentration of the mother-liquor at which a monovariant system was possible, accounts for the many basic nitrates which have been described.

7. That reaction between the higher basic nitrates and water containing nitric acid begins only after some time.

THE CHEMICAL LABORATORY OF
THE UNIVERSITY OF TORONTO,
January, 1901.

A NEW TEST FOR CHLORINE FOR USE WITH THE BLOWPIPE.

BY HENRY W. NICHOLS.

A piece of absorbent paper moistened with a solution of cobalt chloride turns blue when warmed.

A piece of absorbent paper moistened with a solution of cobalt bromide or iodide turns green when warmed.

A piece of absorbent paper moistened with a solution of cobalt nitrate turns a deeper rose color and darkens when warmed.

Paper moistened with solutions of other cobalt salts, when dried in the air, does not turn either green or blue at a temperature below that of the carbonization of the paper.

Paper moistened with a solution of cobalt nitrate and a soluble chloride acts upon warming as if it were moistened with cobalt chloride.

Upon these facts is based the following test for chlorine and for the distinction between chlorine and bromine or iodine. This test calls for such apparatus and reagents only as are commonly used in blowpipe work:

Powder the assay with from one to four volumes of potassium bisulphate. Place the mixture in a closed tube. Moisten a fragment of filter-paper with cobalt nitrate solution and place it in the mouth of the tube. Upon fusing the mixture, the paper under the influence of the hydrochloric acid and sulphuric anhydride given off will turn a bright blue if chlorides are present. If bromides or iodides are present the color will be green. In case of minute quantities it may be necessary to dry the paper before the color appears but ordinarily the sulphuric anhydride evolved by the bisulphate produces the same effect as heating. Although the blue of the cobalt chloride assumes, when faint, a greenish cast, yet it is always distinct from the yellowish-green of bromides. When chlorides and

bromides are found together, the paper turns first blue from chlorine and later green from bromine. If but little bromine is present the final color will be a bluish-green. The test is much less delicate for bromides than for chlorides. If but little chlorine is present and much water condenses in the tube, this water may hold back the hydrochloric acid and should be driven into the test paper. When this occurs it is often necessary to heat the paper to bring out the color, and under these conditions the yellow of the charred paper may produce with the blue a green, somewhat similar to that produced by bromides. Acid potassium sulphate, as purchased, contains too much sulphuric acid and should be fused in platinum until frothing ceases before use; otherwise it froths in the tube in a disagreeable manner. Many bromides contain sufficient chlorine to give a distinct test by this method, a fact that should be remembered when using them for check experiments. The limit of sensitiveness of the test has not been determined. The following tests will indicate its suitability for blowpipe work and mineral determinations: Two specimens of embolite were tested and both the chlorine and bromine were indicated. A specimen of sodalite (Cl, 7.3 per cent) gave a good reaction for chlorine, as did a specimen of zunyite (Cl, 2.91 per cent) with about 25 per cent of gangue. The white crystalline apatite of Snarum, Norway, gave a good reaction while a specimen of the green massive Canadian apatite gave no reaction for the traces (0–0.5 per cent) it generally carries.

Chlorides in solution may be tested by dipping a paper into the solution, spreading a drop of cobalt nitrate solution upon it, drying, and heating. The test thus carried out is not very delicate; moreover, the distinction between chlorides and bromides is obscured, and sulphides and some other substances interfere.

The familiar test for chlorine in the presence of bromine by the generation of chlorochromic anhydride may be advantageously modified for the blowpipe laboratory. In place of the tubulated test-tube a plain test-tube may be used, and in place of the receiver a piece of filter-paper moistened with a saturated solution of sodium carbonate and placed in the mouth of the tube. This alkaline paper retains chromic acid so that

when burned in the forceps the ash will give a chromium reaction with the borax bead. No difficulty will be found in burning the paper while moist, owing to the bromates and chromates present. During the burning the sodium carbonate fuses and collects the ash into a globule which will be a dirty green if it contains much chromium. For the small quantities of material commonly used in mineral testing, a closed tube may be very advantageously substituted for the test-tube whenever the substance tested does not effervesce with acid.

FIELD COLUMBIAN MUSEUM,
February 12, 1901.

ON TRIVALENT CARBON.

(REPLY TO J. F. NORRIS.)

BY M. GOMBERG.

The January number of this JOURNAL[1] contains a paper by Norris and Sanders on "Triphenylchlormethane." They describe a method for the preparation of this compound, which is essentially the same as that published by me some two months previously.[2] Although my paper was presented in full at the Columbus meeting of the American Association for the Advancement of Science, it was given in the Proceedings only by title. This is undoubtedly the reason why the paper escaped the notice of Norris and Sanders before this subject was taken up by them.

In another place[3] I reported the study of the action of metals upon triphenylhalogenmethanes. It was shown in that paper that when silver, mercury, or zinc is allowed to act at ordinary temperature upon triphenylchlor- or brommethane in different solvents, in absence of oxygen, the halogen is removed quantitatively, and there results an extremely unsaturated compound, which, on exposure to air, at once becomes oxidized. The reactions of the resulting oxygen derivative led me to the conclusion that it is best represented by the formula $(C_6H_5)_3C—O—O—C(C_6H_5)_3$; *i.e.*, peroxide of triphenyl-

[1] This JOURNAL, **23**, 54.
[2] *Ibid.*, **22**, 752.
[3] *Ibid.*, **22**, 757.

methyl, while the unsaturated hydrocarbon was assumed to be triphenylmethyl itself, $(C_6H_5)_3C—$, wherein carbon is trivalent.

On p. 58 Norris and Sanders state that metallic sodium has no action on triphenylchlormethane dissolved in ether. On the addition of brombenzene to the solution a reaction took place, and one of the products isolated, while containing no halogen, did not, on analysis, give a sum of carbon and hydrogen equal to 100 per cent. It does not appear quite clear how they "have discovered that an oxygen compound was formed as the result of the action of sodium on a mixture of triphenylchlormethane and brombenzene." This oxygen compound might as well have been the result of the action of *sodium hydroxide*, which was undoubtedly formed to some extent during the three days required for the reaction. Complete exclusion of oxygen-bearing reagents, of the atmospheric oxygen itself, and the subsequent oxidation of the resulting hydrocarbon,—were the proofs necessary to establish the discovery. Nothing of this is mentioned in their paper. They say that this substance resembles the peroxide described by me in melting-point, chemical composition, and solubility, "but further work is necessary before the identity of the two substances can be established." In the second paper[1] not a word is said with reference to this further work. Norris speaks of the oxygen compound as identical with the peroxide described by me. The formation of that body is self-evident in the light of the results published by me. It seems, therefore, strange that Norris should at this stage give up his original problem, the synthesis of tetraphenylmethane, and take up the study of the action of metals upon triphenylchlormethane. I have published only a preliminary paper upon this subject, asking that the field might be reserved for myself. Norris states in the first paper that his problem, while it has a bearing upon my work, is in itself quite distinct. And yet, his whole second paper is devoted to a repetition of my experiments on the action of zinc upon triphenylchlormethane. In my preliminary paper the metals mentioned were sodium, silver, mercury, and zinc; the solvents, benzene, carbon disulphide, and carbon tetrachloride. But, of

[1] This JOURNAL, 25, 117.

course, other solvents and other metals have been tried before and since the publication of the paper. During the past few months particular attention has been paid to this reaction both in ether and acetic ether as solvents. As my results are entirely different from those obtained by Norris, I publish some of them at this time.

At the early stage of this work, absolute ether was frequently employed as a solvent in the reaction of metals upon triphenylhalogenmethane. But, as the substance obtained was shown to contain oxygen, ether was discarded for liquids which do not contain oxygen. It was afterwards shown that the formation of the oxygen derivative does not depend upon the oxygen of the ether, and it was demonstrated that whatever the solvent may be, the reaction is always the same,—the metal removing the halogen from triphenylchlormethane and giving as a result a highly unsaturated hydrocarbon; this was instantly oxidized to an insoluble oxygen compound on exposure to air. The ease with which ether can be removed at low temperatures induced me again to use it in this reaction, with the hope of obtaining the pure, free hydrocarbon. But I noticed that while the reaction proceeded smoothly in many trials, in some instances a dark, thick mass would separate, and in several cases, when zinc was employed, a gas was given off. It was, however, finally shown that the evolution of hydrogen was due to the presence of traces of alcohol or water in the ether. With absolutely dry ether no gas was developed, and by use of this solvent I obtained the triphenylmethyl in large transparent crystals which, on analysis, gave carbon and hydrogen, 99 per cent. Ethyl acetate behaves exactly like ether, but possesses the great advantage that it keeps the zinc chloride formed during the reaction in solution. All the results obtained by Norris are due to the fact that the ethyl acetate employed by him was not pure, and they have no direct bearing upon the question of the valency of carbon.

I. Is Hydrogen Formed in this Reaction?

a. The action of zinc in ethyl acetate.—The ethyl acetate was purified in the following way: The ester (Kahlbaum) was shaken with a solution of sodium carbonate to

remove the acetic acid, and the clear filtrate was allowed to stand for twenty-four hours over a third of its bulk of granulated calcium chloride. It was then distilled and the fraction boiling at 75° to 77° C. was collected separately. This fraction was heated on the water-bath for three hours with phosphorus pentoxide,[1] 100 grams to a liter of the ester. The ethyl acetate was then decanted upon a fresh charge of phosphorus pentoxide and heated for two hours. The liquid was then decanted and distilled. Nearly all came over at the temperature of 76°.4 to 76°.8 C., and the solvent was then fit to be used. Although zinc in any form can be used for this reaction, it is preferable, as will be seen below, to use zinc strips cut of the desired size from ordinary zinc sheet. Strips of about 0.5 x 3 inches are most convenient. The zinc is freed from oxide either by dilute sulphuric acid, or by means of a file or emery paper.

If triphenylchlormethane (1 gram) is dissolved in about 10 cc. of ethyl acetate purified as described above, and the air in the test-tube is displaced by carbon dioxide, then, on dropping in the strip of zinc and rapidly inserting the stopper, the following will be observed: The solution will immediately turn yellow and in a few minutes crystals, which rapidly grow both in size and in number, will appear on the zinc. These large, transparent, pale-yellow crystals are triphenylmethyl itself. This substance, just as in ether, is only slightly soluble in ethyl acetate. Not a bubble of gas will be seen to rise to the surface. I have had occasion to perform this experiment over fifty times with small and large quantities, with both absolute ether and acetic ether, watching the metal for hours through a magnifying glass, and am satisfied that when all the reagents are pure and dry no gas is generated. A solution of these crystals in benzene or in carbon disulphide will rapidly decolorize iodine. On exposure to air the peroxide will be formed. These results, obtained with triphenylmethyl, will be reported later.

The following series of experiments, which were carried out under as nearly the same conditions as possible, show the necessity of employing pure reagents in this reaction. The

[1] P. C. Freer: This JOURNAL, 13, 310.

triphenylchlormethane used was recrystallized from absolute ether and kept in a desiccator provided with soda-lime and sulphuric acid, and in this way was kept free from moisture and hydrochloric acid. In each case 1 gram of the halogen compound was dissolved in 15 cc. of acetic ester placed in a small Erlenmeyer flask provided with a stopper and a calcium chloride tube about 4 inches long. A strip of zinc was then introduced into the solution. The unsaturated hydrocarbon which was formed under these conditions was instantly oxidized to the insoluble peroxide by the dry air entering through the calcium-chloride tube. Occasional shaking facilitates the speed of the oxidation. After a few hours' standing the peroxide was filtered off and thoroughly washed with ether and alcohol. The small amount of the substance adhering to the zinc was scraped off with a spatula, digested with dilute hydrochloric acid, and added to that already collected. The whole precipitate was then washed with dilute acid, water, alcohol, and ether, and dried. As the peroxide is only very slightly soluble in acetic ester and in the other solvents used in this operation, no attempt was made to recover the small amounts lost in this way. The loss amounted to about 25 milligrams. The peroxide was in all cases quite pure, melting at 182° to 185° C.

(1) One gram of triphenylchlormethane, treated as above described in the pure and dry ethyl acetate, gave 0.705 gram of the peroxide. No hydrogen was given off.

(2) Some of the pure ester was shaken with a solution of sodium carbonate, and the clear liquid filtered through a dry filter. The ester was now in the same condition as used by Norris. One gram of the chlorine compound was dissolved in 15 cc. of this solvent. The zinc was at once attacked with strong evolution of hydrogen, but the yield of the peroxide was only 0.050 gram.

(3) Moist ethyl acetate was dried over calcium chloride for one hour. This time the evolution of hydrogen was decidedly less, and the yield of the peroxide was 0.195 gram.

(4) Acetic ester was dried over calcium chloride for five hours. In this case the evolution of gas did not begin till some ten minutes after the introduction of the zinc. It then

proceeded slowly for quite a long time. There is no difficulty in distinguishing, by means of a magnifying glass, the rapidly rising bubbles of gas from the small shining crystals of the peroxide floating through the liquid. The yield of the peroxide was 0.485 gram.

(5) The ester was allowed to stand over one-half its bulk of granulated calcium chloride for twenty hours, and then for five hours longer over a fresh charge of fused calcium chloride. No hydrogen was given off, not a bubble of gas could be noticed, and yet the yield of the peroxide was only 0.550 gram.

(6) The ester from the previous experiment was then treated with phosphorus pentoxide and distilled. Again no hydrogen was formed, but the yield of the peroxide rose to 0.730 gram.

(7) To 15 cc. of the perfectly dry ester 0.1 cc. of absolute alcohol was added. While there was no hydrogen given off the yield of the peroxide showed plainly that the chlorine compound was etherified. The yield was only 0.325 gram. With an ester containing 0.1 per cent alcohol there is an unmistakable evolution of hydrogen.

These results show, it seems to me, quite conclusively that the generation of hydrogen and the formation of the peroxide are not the consequences of one and the same reaction. On the contrary, they are antagonistic to each other; the quantity of one is inversely proportional to that of the other. If, as Norris supposes,[1] the action of metals upon triphenylchlormethane results in the splitting off of hydrochloric acid, and this by its action upon the metal furnishes hydrogen, then the amount of the gas evolved should be proportional to the quantity of the unsaturated hydrocarbon, and consequently to that of the peroxide. But what actually happens is the very opposite. As the increase of the amount of hydrogen and the corresponding decrease of the peroxide seem to depend upon how dry the solvent is, the explanation of what happens is this: The chlorine compound is a very unstable body and is easily decomposed by water. When dissolved in ethyl ace-

[1] A similar theory was advanced by Nef (Ann. Chem. (Liebig), 309, 167) before the publication of my first paper upon this subject.

tate containing some water, it is partially hydrolyzed into triphenylcarbinol and hydrochloric acid, and the latter attacks the zinc. When alcohol is present in the ester, etherification instead of hydrolysis takes place:

$$(C_6H_5)_3C.Cl + H_2O = (C_6H_5)_3C.OH + HCl;$$
$$(C_6H_5)_3C.Cl + C_2H_5.OH = (C_6H_5)_3C.OC_2H_5 + HCl.$$

Nor is it necessary to assume that these changes are instantaneous. The hydrolysis may be only partial, depending upon the relative proportions of water and of the chlorine compound. The equilibrium so established is, however, disturbed as soon as zinc is introduced. As the hydrochloric acid is being used up by the metal, the hydrolysis proceeds further and further. It is evident that the more water there is present in the ester, the more rapid and the more complete is the hydrolysis, and consequently the less peroxide will be formed. Experiments (5) and (7) also show that the acid produced may be too dilute to act upon the zinc at all.

The readiness with which the chlorine compound is hydrolyzed is shown by the following experiment: If absolutely dry halogen compound is dissolved in absolute ether, dry acetic ester, or dry benzene, and a strip of blue litmus paper is introduced into each solution, it will be but a few minutes before the litmus will begin to show an acid reaction. It will turn red, first in the benzene, then in the ether, and last in the ethyl acetate. Apparently there is enough water in the paper to affect the triphenylchlormethane. Hence the acid reaction obtained by Norris[1] in treating the chlor-compound with zinc in moist acetic ester is not at all an indication that hydrochloric acid is split off by the action of the metal.

An attempt was made to measure the degree of hydrolysis by determining the electrical conductivity of the resulting hydrochloric acid. But the acetic ester, like a great many other organic solvents, is almost a perfect non-conductor. The purified and dried ester showed no electrical conductivity when tested with the apparatus at my command.[2] When shaken with a solution of sodium carbonate and filtered through a dry filter, the moist ester also did not show any

[1] This JOURNAL, 25, 120.

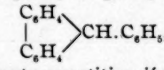
[2] I used a Kohlrausch apparatus with a 20,000 ohm resistance, and no minimum was obtained.

measurable conductivity. A dilute solution of dry hydrochloric acid in dry ethyl acetate, tested as to its conductivity, gave entirely negative results, and yet this solution attacked zinc very readily. To 15 cc. of the dry ester 1 drop of concentrated hydrochloric acid was added; even this solution, although containing traces of water, presented such enormous resistance that its conductivity could not be measured until another drop of water was added. This solution also acted upon zinc with evolution of hydrogen. One-half gram of triphenylchlormethane was dissolved in 10 cc. of the dry ester; no measurable electrical conductivity could be noticed, and the solution gave no hydrogen on the addition of zinc. One-half gram of the halogen compound was dissolved in moist ethyl acetate which had been previously shaken with a solution of sodium carbonate. The solution showed a conductivity of about 0.5×10^{-6}; zinc was acted upon by the solution and hydrogen was formed. A solution of the same concentration in acetic ester which had been dried over calcium chloride only two hours showed no electrical conductivity, but still gave hydrogen when zinc was added. The results from all these experiments show plainly that the amount of hydrochloric acid in ethyl acetate cannot be measured by the degree of the conductivity of the solution; they also show that more than a mere trace of water must be present in order that there should be a measurable conductivity. It is also seen that the readiness of chemical action upon zinc is not at all parallel to the conductivity of the acid in this solvent. Kablukoff[1] showed that the conductivity of hydrochloric acid in dry benzene, xylene, hexane, and ether is very slight. Zecchini[2] has recently shown that dry hydrochloric acid in methyl, ethyl, and amyl alcohol, in acetone, and in ether acts energetically upon zinc; best of all in ether. Apparently the degree of chemical action in these instances is not parallel to that of dissociation; or, perhaps, the conductivity is not in these solvents a reliable measure of dissociation.[3]

[1] Ztschr. phys. Chem., 4, 429. [2] *Ibid.*, 27, 186.

[3] It may be concluded from Experiment 4 that small amounts of hydrochloric acid in tolerably dry ethyl acetate can be detected by the action upon zinc when the electrical conductivity method will fail. Experiment 5 shows that the relative yield of the peroxide is even a more delicate test for the partial hydrolysis of the triphenylchlormethane than the test with zinc.

Norris thinks it probable that, when zinc reacts with triphenylchlormethane, the metal causes the elimination of hydrogen chloride and not that of chlorine alone. Such a loss of hydrogen chloride, according to him, has already been observed, and he cites the experience of Hemilian.[1] Now, E. and O. Fischer[2] proved that when pure triphenylchlormethane is used, Hemilian's diphenylenephenylmethane,



is formed only in minute quantities, if at all. It is only when the chlorine compound contains a considerable quantity of the carbinol that the hydrocarbon in question is produced. Neff[3] came to the same conclusion when triphenylbrommethane is substituted for the chlorine compound. Then again, the temperature of formation, 250° C., precludes any parallelism between Hemilian's reaction and that of the action of metals at ordinary temperatures. E. and O. Fischer justly conclude that Hemilian's body is not the result of a simple molecular rearrangement, but rather that of a very complicated decomposition. Indeed, the temperature is of very great importance in the action of metals upon triphenylhalogenmethane, as is shown by Nef's results.[4] Nef heated triphenylbrommethane in absolute ether with sodium, zinc, and mercury at 60° to 150° C. and obtained a mixture of products, but not triphenylmethyl.

b. The action of zinc in benzene.—When zinc acts upon triphenylchlormethane in benzene no hydrogen is given off. This has been confirmed by Norris. But Norris is of the opinion that the nascent hydrogen in this instance is taken up by the benzene, the latter forming additive products. In support of this view he cites the following experiment: "Sodium was added to ether which contained a small quantity of water, and the amount of hydrogen evolved was noted. Some benzene was now added. The evolution of gas was reduced to almost one-half."[5] It is, however, well known that

[1] Ber. d. chem. Ges., 7, 1208.
[2] Ann. Chem. (Liebig), 194, 259.
[3] Ann. Chem. (Liebig), 309, 168.
[4] *Ibid.*, 309, 169.
[5] This JOURNAL, 25, 121.

of all the aromatic compounds benzene itself is as difficult to reduce as any. Hexahydrobenzene could only be obtained when benzene is heated with a large quantity of hydriodic acid (1.96) at 280° C.[1] Tetrahydrobenzene is not known at all. Dihydrobenzene was obtained by Baeyer[2] from dibromhexamethylene. Why, then, in this action of zinc *all* the hydrogen should be taken up by the benzene does not appear from Norris's experiments. But is it not possible that in Norris's experiment the decrease of the amount of hydrogen simply indicates a retardation of the action of water upon the sodium? On the addition of benzene to ether containing sodium the latter soon gets coated with a gelatinous, transparent layer which protects it from further action. If a fresh piece of metal is now added, the evolution of hydrogen will once more begin, and will continue until this new piece also becomes coated. A fresh addition will once more start the evolution, etc.

I cannot agree with Norris that the action of zinc in benzene is much slower than in other solvents. Norris worked with 1 gram, while the experiments described by me referred to 20 grams of the triphenylchlormethane. Norris simply desired to show that a reaction takes place when ethyl acetate is substituted for benzene, while my object was to show that the abstraction of halogen is quantitative. Hence I thought it best to allow the solution to stand at least five days to insure complete change; but when zinc dust is used with a gram of the material the reaction can be brought to an end in a very short time.

c. Action of mercury on benzene.—The following experiments show conclusively, I believe, that the action of metals does not cause the elimination of hydrochloric acid.

(1) A solution of dry hydrochloric acid in dry benzene was prepared. The strength of the solution was found by shaking 20 cc. of the latter with a solution of silver nitrate and estimating the resulting silver chloride. Ten cc. of the benzene were found to contain 0.0446 gram of the acid. Twenty cc. of this solution were placed in a small Claisen distilling flask,

[1] Wreden: Ann. Chem. (Liebig), 187, 163.
[2] Ber. d. chem. Ges., 25, 1840.

which was connected with a drying tube and a receiver containing a solution of silver nitrate. Fifty grams of mercury were then added, and the flask was allowed to stand several hours, the mixture being shaken occasionally. A stream of dry carbon dioxide was then passed through the solution and the hydrochloric acid not taken up by the metal was in this way driven over into the receiver. The quantity thus recovered was 0.0862 gram. As is seen from this, only 3 mgs. of the acid combined with the mercury under these conditions.

(2) Two grams of triphenylchlormethane were dissolved in 20 cc. of dry benzene, which contained no acid, the solution was placed in a dry Claisen flask, connected as before with a receiver containing a solution of silver nitrate. Fifty grams of mercury were added and the mixture was allowed to stand several hours. A stream of perfectly dry carbon dioxide was then passed through the solution for twenty-four hours. The silver nitrate solution showed at the end of that time only a slight turbidity, and yet the filtered benzene solution furnished on exposure to air 0.9 gram of the triphenylmethyl peroxide. Had the metal caused elimination of hydrochloric acid from the halogentriphenylmethane, there should have been formed in this experiment 0.1278 gram of the acid. It was shown above that mercury was only slightly attacked by hydrochloric acid in benzene; consequently, had there been any hydrochloric acid formed in this experiment at all, a large amount of it should have been found in the receiver.

(3) The question may well be asked, whether the chlortriphenylmethane or the resulting triphenylmethyl, does not exert some catalytic influence, causing the hydrochloric acid to act upon the mercury. In order to test the theory, the experiment described under (2) was repeated, substituting, however, benzene containing hydrochloric acid for the pure solvent. Of the 0.0892 gram of acid introduced, 0.0822 gram was found in the receiver, as compared with 0.0862 gram obtained in the blank experiment (1). The loss of the 0.004 gram of the acid is easily accounted for by the more finely divided state of the mercury caused by a change in the surface-tension of the metal. A somewhat larger surface was exposed and the action of hydrochloric acid proceeded

with a proportionately greater velocity. The benzene solution gave on exposure to air 1 gram of the peroxide, which should have been accompanied by 0.142 gram of hydrochloric acid. Yet none of this additional acid was found in the receiver. No doubt, none was formed.

d. Action of concentrated sulphuric acid.—The action of concentrated sulphuric acid upon triphenylchlormethane is also considered by Norris as a proof that the metal causes the elimination of hydrochloric acid from the halogen compound, and not that of halogen alone. He found that on dissolving triphenylchlormethane in concentrated sulphuric acid large quantities of hydrochloric acid are given off. The observation is correct, but there is no analogy between this reaction and that of metals upon the halogen compound. Benzalchloride and benzotrichloride react with sulphuric acid with the evolution of hydrochloric acid, and the acid sulphates so formed are easily hydrolyzed. This forms the basis of the patented methods for the manufacture of benzaldehyde and benzoic acid.[1] The reaction in the case of triphenylchlormethane is no doubt perfectly analogous, being probably this:

$$(C_6H_5)_3C.Cl + H_2SO_4 = (C_6H_5)_3C.OSO_3H + HCl;$$
$$(C_6H_5)_3C.OSO_3H + H_2O = (C_6H_5)_3C.OH + H_2SO_4.$$

One gram of the halogen compound was dissolved in 10 cc. of sulphuric acid, and the clear yellow solution was poured into water. The snow-white, flocculent triphenylcarbinol thus obtained melted at 154° to 158° C. 0.925 gram was obtained in this way, while the theoretical quantity is 0.934 gram, making a yield of 99 per cent. This may prove to be the best method for the preparation of triphenylcarbinol.

II. Does Dry Oxygen Give the Peroxide?

It is known that certain chemical reactions do not take place when all traces of water are completely excluded. Some assume that slow oxidation by the atmospheric oxygen also requires at least traces of moisture. Traube's theory, that oxidation in general is never effected directly by molecular oxygen, but always through the intervention of water, is

[1] V. Meyer and P. Jacobsen: Lehrbuch, II, pp. 479 and 537.

also accepted by Nef. Nef[1] could not oxidize dry benzaldehyde to benzoic acid by perfectly dry oxygen. Jorissen,[2] however, could not confirm these results. Engler and Weisberg[3] succeeded in oxidizing turpentine when all possible traces of moisture were rigidly excluded. Whichever theory is accepted as to the part that water plays in all cases of slow oxidation, or *autoxidation*, one fact is established beyond any doubt: *molecular* oxygen never oxidizes water to hydrogen peroxide, a substance which has been shown to occur in a large number of instances of autoxidation of metals and of many organic compounds. The different theories which attempt to explain its formation—those of Schönbein, Traube, and Engler—all agree on this point: It is never the result of the direct oxidation of water by the molecular oxygen. According to Norris, the unsaturated hydrocarbon, which is formed by the action of zinc upon triphenylchlormethane, has the constitution $(C_6H_5)_2C:C_6H_4$. Such a body could, he states, give rise to the peroxide,

$$(C_6H_5)_2C—O—O—(C_6H_5)_2C,$$

by the combined action of oxygen and water, or by the action of hydrogen peroxide; hence water is absolutely necessary for this reaction. But then, the water cannot form hydrogen peroxide unless the hydrocarbon itself is first oxidized directly by the atmospheric oxygen, a part of which becomes in this way what is known as "active" oxygen, and is then capable of oxidizing water or some other "acceptor." The reaction must be represented as follows:

$$\text{Hydrocarbon} + (O=O) + H_2O = (\text{Hydrocarbon} + O) + H_2O_2 \quad (I).$$

The hydrogen peroxide in its turn gives rise to the reaction:

$$2(C_6H_5)_2C:C_6H_4 + H_2O_2 = (C_6H_5)_2C—O—O—(C_6H_5)_2C \quad (II).$$

We thus reach the conclusion that if hydrogen peroxide causes the formation of triphenylmethyl peroxide (II), the necessary hydrogen peroxide can only result from a direct oxidation of another portion of the unsaturated hydrocarbon

[1] Ann. Chem. (Liebig), **298**, 280.
[2] Bodländer: "Ueber langsame Verbrennung," p. 83.
[3] Ber. d. chem. Ges., **31**, 3049.

by the atmospheric oxygen (I). But it was shown above that the yield of the triphenylmethyl peroxide is 80 per cent of the theoretical quantity. Consequently, the remaining 20 per cent must have taken up a quantity of oxygen equal to that which combined with the water to form the hydrogen peroxide for the use of the remaining 80 per cent of the hydrocarbon. In other words, there ought to be formed in addition to the insoluble triphenylmethyl peroxide another product very much richer in oxygen, supposing even that all the hydrogen peroxide is used up in the formation of the triphenylmethyl peroxide. I have been at work for some time trying to determine what becomes of the remaining 20 per cent of the triphenylmethyl. I find some triphenylmethane, some triphenylcarbinol, and a portion which cannot be brought to crystallization. It remains, however, to determine whether all these products are formed before or during the oxidation of the unsaturated hydrocarbon.

But aside from the theoretical considerations it is not difficult to prove experimentally that the hydrogen peroxide theory, or even the simple theory of the combined action of oxygen and water, is not correct. The reaction,

$$2(C_6H_5)_2C:C_6H_4 + H_2O + O = (C_6H_5)_2C{-}O{-}O{-}C(C_6H_5)_2,$$

implies that a certain quantity of water must be used up in the formation of the peroxide. The production of 1 gram of the peroxide represents a disappearance of 0.0354 gram of water. This is certainly a weighable amount, and can be excluded if desired. Accordingly, Norris was unable to obtain the peroxide when dry air was drawn through a benzene solution of the compound for twenty minutes. I have had occasion to make the peroxide a great many times, and have never failed to get it by the use of air which was passed through a drying train such as is used in elementary analysis. The comparative yields of the peroxide with moist and dry ethyl acetate as a solvent were obtained, it will be remembered, by the use of dry air. The following experiments, however, show conclusively that water does not enter into the reaction as such:

Three grams of pure and dry triphenylchlormethane were

dissolved in ethyl acetate which had been thoroughly dried over phosphorus pentoxide and placed in a small Drechsel bottle (Fig. 1). The joint in the neck was carefully ground

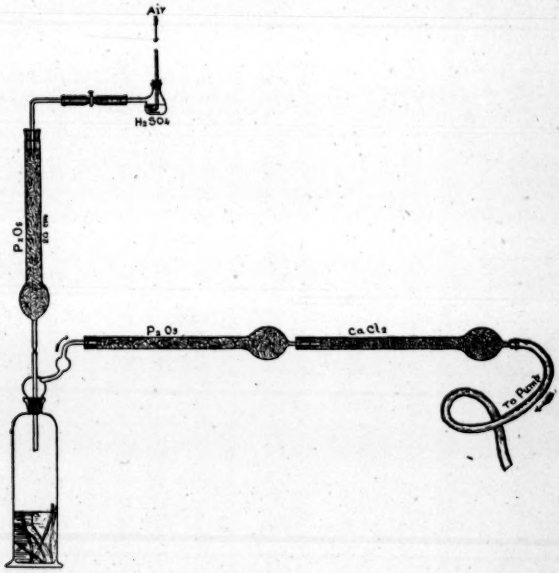


Fig. 1.

and was shown to be air-tight. The apparatus was first dried by heating it with a naked flame and exhausting, and then allowing air, which was passed in a slow stream through sulphuric acid and phosphorus pentoxide, to enter the flask. This treatment was repeated ten times. The solution of the halogen compound and a few strips of zinc were then introduced. The reaction began at once, and no evolution of hydrogen could be detected. A slow stream of dried air was passed over the solution from the very beginning of the reaction by means of a suction pump, care being taken to prevent backward diffusion of moisture as shown in the sketch. The

triphenylmethyl peroxide began to form at once, and the precipitate kept on increasing as the reaction proceeded. After a day's action 2.050 grams were obtained, which is 73 per cent of the theoretical amount. The experiment was repeated with 5 grams, and this time the air was passed into the solution of the halogen compound. The yield was 3.650 grams, which is 78.5 per cent of the theoretical quantity. In this last instance there should have been used up 0.128 gram of water, which is far from a negligible quantity, and was certainly excluded by the conditions of the experiment.

It might be said that perhaps the zinc chloride formed in

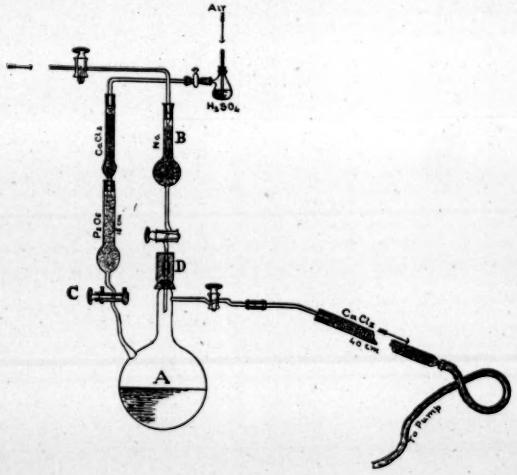


Fig. 2.

the reaction causes a condensation of some acetic ester with the formation of small amounts of water. In the following experiment any such possible errror is entirely eliminated. A solution of triphenylchlormethane in benzene, which had been standing over zinc six weeks, and was thus completely converted into triphenylmethyl, was siphoned over into the perfectly dry flask, *A* (Fig. 2). Although during the reaction 6

grams of zinc chloride were formed, and the benzene, therefore, must have been dry, still, in order to insure complete absence of moisture, the solution, before entering the flask *A*, was allowed to remain in contact with a large amount of metallic sodium in tube *B* for one-half hour. The stop-cocks were specially ground, stop-cock, *C*, having in addition a mercury seal. The rubber connection at *D* was entirely under mercury, and the remaining rubber connections were heavily paraffined. A slow stream of air was then allowed to enter the flask. As soon as the carbon dioxide was displaced the insoluble peroxide began to crystallize on the surface of the perfectly clear benzene solution. In a few hours the reaction was finished, and the filtrate from the peroxide gave no further precipitate on exposure to moist air. In this case, as in the two experiments with acetic ester, the oxidation was complete even when perfectly dry air was used. The quantity of the peroxide obtained in the last experiment was 5.100 grams. This, according to the theory of Norris, means an absorption of 0.1805 gram of water. No such amount of moisture could have been present.

It is of course possible that in all the experiments described, a minute trace of moisture was still present, and the oxidation was done through the catalytic influence of water. But this is a question of an entirely distinct nature and need not be discussed here. One or two molecules would suffice for the purpose of catalysis, and, as V. Meyer observed long ago,[1] we can never reach such a perfection in manipulation as to insure the absence of such minute traces of water.

The peroxide is therefore formed by the action of oxygen alone upon the unsaturated hydrocarbon. If the constitution of the peroxide is that which I have ascribed to it,

$$(C_6H_5)_3C—O—O—C(C_6H_5)_3,$$

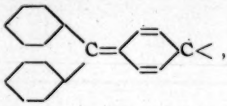
then the unsaturated hydrocarbon cannot be $(C_6H_5)_3C : C_6H_4$.

III. Is the Unsaturated Hydrocarbon Colored?

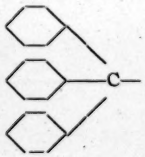
Should it be proved at some future time that the action of metals upon triphenylchlormethane results, after all, in the elimination of hydrochloric acid, the behavior of the hydro-

[1] Ber. d. chem. Ges., 23, 395.

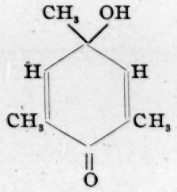
carbon will best be explained by the constitution,

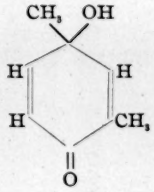


which is a modified form of Nef's[1] hypothesis, that of $C_6H_4—\overset{\downarrow}{C}=(C_6H_5)_2$, and not, as Norris assumes, by one in which the methane carbon atom is linked to 2 carbon atoms in a single benzene ring. The first formula would explain the extreme unsaturation of the hydrocarbon, while that of Norris implies a structure containing a tri-, tetra-, or pentamethylene ring, and the compound, therefore, should be fairly stable. But, for the present at least, we must assume that the metals remove only the halogen from triphenylchlormethane, and the resulting body must have, it seems to me, the constitution



The modified formula of Nef implies a half-quinoid structure. Compounds of such a constitution need not, however, be colored, as is shown by the recent work of Bamberger[2] on quinols. Thus mesitylquinol and dimethylquinol





are colorless.

[1] Ann. Chem. (Liebig), **309**, 166.
[2] Ber. d. chem. Ges., **33**, 3600.
[3] *Ibid.*, **33**, 3637.
[4] *Ibid.*, **33**, 3647.

It is nevertheless important to determine definitely whether the hydrocarbon under consideration is colored or not. Many attempts were made for that purpose, especially since the publication of the paper by H. Kauffmann,[1] who ascribes to triphenylmethane a tendency towards the quinoid structure on physical grounds. By precipitating the hydrocarbon from a benzene solution by means of absolute ether it is possible to obtain crystals of only very pale-yellow color, which on standing become darker. It need not necessarily follow from the fact that the solutions are always yellow that the pure substance itself must be colored. The color of the solution may be due either to an intermediate oxidation product of the hydrocarbon or to some accompanying impurities. By dissolving in carbon disulphide the pale-yellow crystals formed with acetic ester as a solvent, and precipitating with acetic ether, I obtained the crystals perfectly colorless. It is my intention to test this result in several different ways before it can be considered as settled.

In conclusion, I wish to state that this work will be continued, and I ask again that the field may be reserved for myself for a while longer.

CHEMICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
February 28, 1901.

REPORTS.

International Atomic Weights (II).

It is of interest to note in connection with the report of the Committee of the German Chemical Society (which has already been reviewed in this Journal, Vol. 24, p. 377) that several other countries and organizations have decided in favor of adopting as the standard of atomic weights the value O = 16.000. The chemists of France, who had not expressed their opinions at the time of the last report, declared themselves in favor of this standard at the Congress of Applied Chemistry, in Paris, in 1900, and the Swiss Committee has joined the movement. Fully as important is the very emphatic declaration of the Deutsche electrochemische Gesellschaft, who announce their determination to adhere to O = 16, because of its relation to the electrochemical equivalent, whatever the pure chemists may decide to do.[2]

[1] Ber. d. chem. Ges., **33**, 1725.
[2] Ztschr. anorg. Chem., **25**, 341 (1900).

It is both singular and unfortunate that the most serious opposition to the movement is to be found in Germany itself, the birthplace of the desire for uniformity. The report comes that Wislicenus, Winkler, Erdmann, and the other well-known adherents of O = 15.88 (or H = 1)[1] have found a large following among the teachers in Gymnasia and Realschulen. While undoubtedly the teacher's side of the question is an important one, it is only one side of a matter with manifold relationships. Of course, if in the new standard O = 15.88 really presents great advantages to the teacher (a supposition which may well be doubtful), and if in consequence all men who are primarily teachers should vote for this new standard, the numerical majority would be overwhelming in its favor because of the predominance of teachers. Nevertheless this overwhelming majority would represent only a single point of view, and the importance of this single point of view in relation to the more purely scientific aspects of the matter is a question worthy of debate.

When the letters asked for by the German Committee have been published, we shall have further light upon the subject, but for the present the published majority is very strongly in favor of O = 16.000. Whatever may be the outcome, one hopes that the whole world may accept it, for uniformity and stability are advantages which will in time be seen to outweigh all other arguments on either side of the question.

January 5, 1901. T. W. R.

The Higher Superoxides of Hydrogen.

Since the note on this subject appeared in this JOURNAL, two criticisms of Bach's work and his answer to them have appeared. Armstrong[2] claimed that Bach had failed to take into account the existence of persulphuric acid in his mixture of hydrogen peroxide and sulphuric acid, which would account for the abnormal evolution of oxygen when such a mixture is titrated with potassium permanganate, and that further, the hydrogen peroxide which he obtained from the peroxides of the metals, probably also contained persulphuric acid. Again, Bach regarded the fact that other dehydrating agents besides sulphuric acid, when mixed with hydrogen peroxide, produce effects similar to those obtained in using Caro's reagent, as evidence that hydrogen peroxide is converted into

[1] The adherents of this standard are inclined to consider themselves conservatives, and maintain that they are preserving the old order of things. On the other hand I am inclined to call any standard of measurement a new one which changes the numerical magnitude of all the values measured by the standard.

[2] Proc. Chem. Soc., 1900, 134.

hydrogen tetroxide by dehydration. Armstrong pointed out that the effects produced by Caro's reagent are merely such as would be expected from the action of hydrogen peroxide in the presence of a strong dehydrating and hydrolyzing agent, so that it is unnecessary to assume the existence of any new compound to explain them.

Berthelot[1] found that when he treated a solution of hydrogen peroxide and sulphuric acid with potassium permanganate in sulphuric acid, both solutions being cooled to —12° C., until there was no further decoloration, there was no effervescence. When the mixture was removed from the refrigerant and shaken, there was a rapid evolution of gas. He explained these phenomena by saying that hydrogen trioxide, H_2O_3, was formed which was stable only at low temperatures and decomposed with the evolution of oxygen as soon as it was removed from the refrigerant.

Baeyer and Villiger[2] repeated the experiment of Berthelot and found that the phenomenon observed was merely one of supersaturation. If hydrogen trioxide was formed in Berthelot's mixture, then it should not be decomposed by shaking at the temperature, —12°, at which it was formed. However, when Baeyer and Villiger repeated the experiment, they found that when the solution was shaken at —12° the theoretical amount of oxygen was evolved, and was the same in quantity as when the potassium permanganate and hydrogen peroxide reacted at +15°. The only difference between the actions at the two temperatures was that at the lower temperature the oxygen was evolved only half as rapidly as at the higher. In both cases the same, theoretically correct amounts of oxygen were liberated. On the strength of this experiment the authors claim that the experimental evidence in favor of the existence of hydrogen trioxide is of no value.

Bach[3] recently published results of the action of potassium permanganate on Caro's acid, which led him to think that the latter contained hydrogen tetroxide. Baeyer and Villiger[4] have also repeated his experiments, and while they admit his observations to be correct, they do not accept his interpretation of them.

Bach found that when a mixture of hydrogen peroxide and sulphuric acid in such proportions as to contain Caro's acid and an excess of the peroxide, was treated with potassium permanganate, the amount of oxygen evolved was more than twice as much as would be normally evolved from the permanganate alone.

[1] Ann. chim. phys., [5], **21**, 176.
[2] Ber. d. chem. Ges., **33**, 2488.
[3] *Ibid.*, **33**, 1506.
[4] *Loc. cit.*

As he had worked with a mixture of hydrogen peroxide and Caro's acid, Baeyer and Villiger first tried the action of potassium permanganate on Caro's acid alone, which was prepared by mixing together potassium persulphate and concentrated sulphuric acid, pouring the mixture on ice, and diluting. They showed that this acid was free from hydrogen peroxide. It was shown by them that no reaction takes place between potassium permanganate and pure Caro's acid in acid solution. However, they did confirm Bach's results in regard to the evolution of an amount of oxygen greater than that called for by the theory when a mixture of hydrogen peroxide and Caro's acid is treated with potassium permanganate, but they explain this abnormality in a different way.

They attribute it to a catalytic decomposition of Caro's acid, due to the presence of manganous sulphate. They claim that as soon as a small amount of potassium permanganate is reduced, the manganous sulphate thus formed is oxidized to manganic sulphate, and that this then acts catalytically on Caro's acid, causing its decomposition and liberating oxygen. Baeyer and Villiger also found that an excess of manganous sulphate does not act as well as a small amount in decomposing Caro's acid, hence in the reaction between potassium permanganate, hydrogen peroxide, and Caro's acid, a maximum is reached in the decomposition of Caro's acid, as soon as manganous sulphate is formed in too large a quantity. These results then appear to destroy the experimental foundation for the existence of hydrogen tetroxide.

In concluding their paper, Baeyer and Villiger discuss the three views of the action of potassium permanganate on hydrogen peroxide.

According to Schönbein, the permanganate and the peroxide simultaneously evolve atomic oxygen which then condenses to molecular oxygen. Hydrogen peroxide would thus appear to be an oxidizing agent, while in all its other reactions it is a reducing agent. Further, Caro's acid ought to react all the more easily with potassium permanganate, while, as a matter of fact, it does not react at all with it.

Berthelot's view is that the peroxide is first oxidized to the trioxide, which then breaks down into water and oxygen. Baeyer and Villiger have shown his views to be erroneous.

The most probable view seems to be that of Weltzien and Traube, according to which the permanganate oxidizes the hydrogen of the peroxide to water, while the oxygen is set free. Thus all of the oxygen liberated comes from the peroxide. The fact that Caro's acid does not react with potassium permanganate does not stand in opposition to this view, since in other cases easily oxidizable hydrogen is rendered

more difficultly oxidizable by union with a negative group, as is seen on comparing the behavior of phosphine, hypophosphorous acid, and phosphorous acid.

In answering Armstrong's criticisms that his solutions of normal sulphuric acid and hydrogen peroxide might have contained some persulphuric acid, which then caused the excess of oxygen to be evolved, Bach[1] calls attention to the fact that in his check experiments with potassium permanganate and hydrogen peroxide diluted with normal sulphuric acid, amounts of oxygen were always evolved closely approximating the theoretical amounts, but never exceeding them. Thus Armstrong's criticism seems to be met.

With reference to the criticisms of Armstrong as well as of Baeyer and Villiger of his work with Caro's acid, Bach lays stress on the fact that he was working with a concentrated Caro's acid, while Baeyer and Villiger always worked with a dilute acid.

Baeyer and Villiger claimed that Caro's acid would not react with potassium permanganate and that hence the decomposition of the acid must be catalytic. Bach, on the other hand, found that concentrated Caro's acid reacted very readily with strong potassium permanganate. He was able to titrate potassium permanganate, dry or in solution, in concentrated sulphuric acid with concentrated Caro's acid, and by measuring the oxygen evolved found it to be in accord with the theory. Further, he showed that concentrated Caro's acid was not decomposed by manganous sulphate at ordinary temperatures, nor by the solution after titration with potassium permanganate. Hence, he concludes that the excess of oxygen which he obtained in his first experiments comes from a higher persulphuric acid $(HO_3S.O.O.SO_3H)_3$, which contains an active oxygen atom and which yields twice the theoretical amount of oxygen when titrated with permanganate. When working with the compound $H_2SO_4 + H_2O$ partial hydrolysis takes place with the splitting off of sulphuric acid, H_2SO_4, and the formation of tripersulphuric acid, $(HO_3S.O.OH)_3$, the concentrated Caro's acid, which, upon further dilution, breaks down into simple molecules of monopersulphuric acid, $HO_3S.O.OH$, and this reacts only slowly with potassium permanganate and is susceptible to catalytic decomposition. That concentrated Caro's acid contains three oxygen atoms united to one another follows from an observation of Bamberger that dilute Caro's acid neutralized with potassium carbonate and heated with a catalyser yields ozone.

[1] Ber. d. chem. Ges., 33, 3111.

Bach thinks that his views on Caro's acid are as fully justified as are those of Baeyer and Villiger, only his apply to the concentrated acid, while theirs apply to the dilute.

C. E. C.

A Recent View of Atomic Structure.

Recent observations[1] on electrically charged gases have necessitated a change of views in regard to the ultimate divisibility of matter. These new conceptions apply as yet only to gases, and they are based wholly upon physical studies. The subject is, however, of great interest to the chemist, as the atom is his unit, and anything that goes to show that this is capable of subdivision, strikes at the foundations of chemistry. Much of the work which has led to these interesting results has been done by Prof. J. J. Thomson, who has devised many experiments to clear up doubtful points. Some experiments have been made which show that the molecules of a gas and the particles of the same gas which carry the electrical charges, when a current is passed through it, are not of the same size or nature. It has been shown that there is a striking analogy between a dilute solution of an electrolyte and a gas exposed to the Röntgen rays, and that these rays have the power to dissociate the gas into its oppositely charged ions. Such a dissociated gas is a conductor and will rapidly discharge a charged metal plate, while a gas under ordinary conditions and protected from all influences which can cause dissociation, can come in contact with an insulated charged metal plate without removing any of its charge, although myriads of its molecules come in contact with the plate, whose unit surface contains only such a charge as could be carried thousands of millions times by a cubic centimeter of hydrogen.

That the electrified particle, under ordinary conditions of pressure, is more complex than the molecule is indicated by a result obtained by Mr. Townsend, who found that electrified hydrogen does not diffuse through a porous cup as rapidly as the same gas in the ordinary conditions—a fact probably due to the aggregation of the particles about one as a nucleus. Another point in favor of the view that the ordinary gas differs from the charged one is that, whenever a gas becomes a conductor when heated, it can be shown, by purely chemical means, that chemical decomposition has been caused by the heat and that the conductivity is not due to the increase in temperature. Such an action occurs when the gas is split

[1] The Discharge of Electricity through Gases, J. J. Thomson, 1898. Les Rayons Cathodiquis, P. Villard, 1900. Phil. Mag., 44, 293; 46, 528; 48, 547. Phil. Trans., 193, 129 (1896).

up into atoms by heat; but when it is broken up into simpler molecules and not into atoms it does not show the conductivity.

The figures given for the absolute size of the molecules of gases are so uncertain that no correct idea of the absolute charge can be gained in this way; but a method has been devised which will probably give a more correct value. When an electrified gas is admitted into a vessel containing water vapor, even if the gas in the vessel is not saturated, a fog is formed, and from a knowledge of the number of water particles, which can be determined, and the total charge, the atomic charge can be determined. That the current is carried through the gas by the movement of oppositely charged particles, was shown in the following way: Two tubes containing electrodes, placed about 2 mm. from the ends of the tubes, were introduced into a vessel containing water, and bent in such a way as to bring the ends of the two tubes about 2 mm. apart. The other ends of the tubes were inserted under test-tubes to collect the gas formed. When the air had been driven out of the vessel and the water heated until it was filled with the vapor, a current was passed and the gases formed were driven up the tubes by the steam. When the gas collected was exploded to remove the hydrogen and oxygen, which were present in the proportions to form water and which had been formed along the spark, there remained in the tubes an excess of gas which in one tube was mostly hydrogen and in the other mostly oxygen, and in amount these bore a similar relation to the amount of electricity which had been passed through the vapor. We thus see that the passage of the current through the gas is due to the oppositely charged ions, and it has been shown that the gas can be rendered a conductor by the action of light, Röntgen rays and heat which serve as dissociating agents.

A study of the phenomena occurring when the current is passed through a tube exhausted to a fraction of a millimeter showed that under the conditions of the experiment there is a formation of rays with properties different from any before observed. From the fact that these appeared to start from the cathode they were called cathode rays and were supposed by Goldstein and later by Wiedemann, Hertz, and Lénard to be due to waves in the ether. This so-called "ether theory" was accepted by many as it sufficed to explain the phosphorescence, and mechanical and heating effects; but the peculiar action of the rays in a magnetic field could not be explained unless it was regarded as *sui generis*. In order to explain this and other facts Crookes suggested that the rays consist of

minute particles of matter charged with negative electricity and moving at a high velocity. For a time both the "ether theory" and the "corpuscular theory" had their supporters; but at the present time the latter is the one generally accepted. The advocates of the former theory would not grant the possibility of the particles penetrating solid matter and passing through unchanged, while the opponents pointed out that no case was known in which vibrations of the ether behaved as these rays did in a magnetic field. In high vacuo the passage of the rays can be traced by the phosphorescence inside the tube and on the glass.

The rays render many substances, as the diamond, ruby, calcium fluoride, barium platinocyanide, etc., phosphorescent, and such bodies then emit the Röntgen rays. The mechanical effects of the cathode rays can be shown by their action upon small vanes mounted in the tube on an axis so that the rays strike the tops of the vanes as they are revolved by their action. The heating effect of these rays is so great that a piece of platinum iridium mounted at the focus of the rays can be heated to the fusing-point, and the surface of a diamond can be converted into graphite, indicating a temperature of at least 3600°. These effects can be explained as due to radiant energy comparable to light or to the shock of material particles moving with great velocity. These rays are charged with negative electricity, and it is impossible to change the path of the rays without changing the course of the negative electrification. The rays are deflected by an electrostatic field, and passage between two plates whose potential difference is as little as 2 volts will produce this result. In a given magnetic field, with a given potential difference between the terminals, the magnetic deflection is the same in all gases, the similarity extending to the slight details. The phenomena manifested by these can be satisfactorily explained, according to Thomson, by considering them to be particles of matter carrying a negative charge. Properties of the rays, based on this conception, can be predicted, and they have been found upon investigation to agree with those predicted.

In order to get some idea of the probable size of the particles, Thomson studied the action of the rays on a thermo-electric junction and, from the observations made here and a knowledge of certain necessary data, he was able to determine the value of m/e, where m is the mass and e the charge. As the value of m/e as thus determined was found to be 1/500 of that of hydrogen, which is 10^{-4}, in the case of the ordinary electrolysis of liquids and gases, either the value of e must be much greater than that carried by an ion of an electrolyte, or

the value m of the corpuscle must be very small as compared with that of the ion.

Whether the small value of m/e, which was found to be entirely independent of the nature of the gas and of the electrode, was due to e being greater or m smaller than the value of these for the ion in electrolysis was not determined until it was shown that the value of m/e for ultraviolet light and for the negative electrification produced by an incandescent carbon filament were the same as in the cathode ray, and that a direct determination of the value of e gave a value which was the same as the charge carried by the hydrogen ion in the electrolysis of solutions. As the value of e is therefore the same, the value for m, or the mass, is much smaller than the atom, being about 1/1000 that of the hydrogen atom.

Professor Thomson thinks that the passage of the current through the gas, which is at a low pressure, causes a breaking off of a part of one or more atoms, the part broken off having a unit charge of negative electricity and being very small as compared with the part left behind which takes a positive charge, and is comparable to a mass of ordinary atoms, so that the particle which escapes with the negative charge is a small part of an atom perhaps of a mass. This, with the other evidence, leads to the assumption that the atom is composed of corpuscles and holes, the latter predominating, so that in a gas at low pressure there would be little probability of these corpuscles colliding, and they can, on account of their small size and great velocity, which is about 40,000 kilometers per second, penetrate the intramolecular spaces of solid bodies, especially as the mass of these particles is only about $3/10^{-26}$ of a gram.

This corpuscle may be the fundamental quantity in terms of which all electrical processes can be explained, as its *mass* and *charge* are invariable and independent of the *method of its formation* and of the *gas* which is present in the tube.

This conception as to the presence of corpuscles in atoms might be regarded as evidence in favor of the view held by Prout and others regarding the presence of primordial atoms in all substances, but Thomson points out that this could not be due to hydrogen as Prout supposed, as all the evidence seems to show that the size of the corpuscle is very small as compared with the hydrogen atom.

When changes in the electrical charge of an atom occur, they are due to the movements of corpuscles from the atom, when the positive charge is increased, and to the atom when the negative atom is increased. The liberation of anions and cations in electrolysis of solutions consists in the pas-

sage of a corpuscle from the electrode to neutralize the positive charge and one from the ion to the electrode to neutralize the negative charge of the ion. Accordingly, the mass of the atom is not invariable, and when hydrochloric acid is electrolyzed we have ions of hydrogen in which the mass of the atom is less than half the mass of the hydrogen molecule, H_2, and that of chlorine greater than half that of the chlorine molecule, Cl_2. Thomson thinks that not more than one corpuscle is broken off from any one atom, but that methods may be discovered which will enable us to set all the corpuscles free.

Although these particles cause a marked chemical action in a number of cases, it is impossible to isolate and collect them as the amount formed is so slight. Thomson has calculated that with the coil which he used for the experiments, running night and day for a year, the amount produced would be only *one three-millionth of a gram*. Goldstein has shown that the haloid salts of the alkaline metals are colored by the cathode rays as are those of silver, lead, and mercury. This change in color can be observed for several months if the material is kept in the dark, but exposure to light, and especially heating, restores the color. In the former cases it has been shown that a liberation of halogen takes place and that the absorption spectra of these substances are identical with the spectra of the halides which have been exposed to the vapors of the metal. The salts thus reduced show great photographic activity, and in some cases substances that have been exposed to the rays become luminous at a point far below that at which they ordinarily show the same properties. The rays, in general, act as reducing agents, as can readily be shown by exposing a silicate, rich in lead silicate, to the rays, when rapid reduction, even in the interior of the crystal, takes place. When copper silicate, which is clear and colorless, is exposed to the rays there is a formation of a red cuprous compound. Glass often becomes dark when exposed to the rays as it does when exposed to the action of the reducing flame. J. E. G.

Combustible Gases in the Atmosphere.

In a recent number (January, 1901) of the Annales de Chimie et de Physique there is a summary of the results obtained by Gautier during an investigation which has been in progress for a number of years upon the combustible gases of the air and the presence of hydrogen as a constituent of the atmosphere. The careful attention to details and the thoroughness of the work as well as the methods, which have been used to overcome obstacles, especially impresses one who studies these results. Before this work could be taken up it

was necessary to test the accuracy of the methods which had been suggested for the detection and determination of the gases to be studied, and in some cases to determine the exact conditions which would give the correct results. In order to determine with great accuracy the amount of combustible gases in the air, by converting them into carbon dioxide and water, it was first necessary to remove all the acid gases and moisture, a result which is not as simple as it appears *a priori*.

It was found impossible entirely to remove the carbon dioxide from a gas in which it was present in amounts less than $\frac{1}{100000}$ of the total gas, by passing it through a solution of potassium hydroxide; but if this was then passed through a tube containing crystallized barium hydroxide the last trace was easily removed. In order to remove the moisture he found it necessary to pass it through a small quantity of pure sulphuric acid, which had been boiled, and then over phosphorus pentoxide which had been saturated with oxygen at 260°. A careful examination showed that no appreciable amount of the sulphuric acid vapor was carried off by the gas under the conditions used.

A number of the methods which have been suggested for the determination of carbon monoxide were found to be inaccurate and not sensitive if the carbon monoxide was present only in small quantities; but one method was worked out which makes it possible to estimate carbon monoxide rapidly and accurately, when mixed with 10,000 to 20,000 times its volume of air. The reaction which takes place and which is complete at 65° to 75°, whatever the dilution of the gas may be, is represented by the following equation:

$$5CO + I_2O_5 = 5CO_2 + I_2.$$

If it were practicable to determine the amount of carbon dioxide formed, 1 part of the monoxide to 100,000–300,000 of air could be detected by this reaction. It was also shown that this great accuracy could be secured even in the presence of other gases present in the atmosphere, as these gases do not act on the pentoxide of iodine at the temperature of the reaction.

By the methods which have been described Gautier was able to remove the acid gases, as well as water and carbon monoxide, and was then in a position to study the methods that could be used for the detection and determination of the hydrocarbons and hydrogen in the air.

When hydrogen at a dilution of $\frac{20}{100000}$,—about that in which it is present in air,—is passed over a layer of copper oxide about 70 cm. long, at the rate of 2 to 3 liters per hour, it is com-

pletely oxidized; but if the layer of oxide is only 30 cm. long, only about 70 per cent of the hydrogen is oxidized. When a mixture of hydrogen and hydrocarbons is passed over the copper oxide, the hydrogen is oxidized first and the hydrocarbons are changed into hydrocarbons which are more difficult to oxidize. This necessitates the use of a layer of the oxide 80 cm. long to oxidize the gases completely. Experiments with mixtures of copper oxide with other oxides and platinum sponge gave no better results. It was also found that after long use the oxide will partly oxidize the hydrogen, but will not act at all on the hydrocarbons. Special forms of absorption apparatus and a furnace, in which the temperature could be carefully regulated, were used in this work.

By a comparison of the results obtained with the air of the city, of the country, of high snow-covered mountains where great privations were suffered in order that the air might not be contaminated by the products of combustion from a fire, and of the sea, it was shown that hydrogen is present in the atmosphere to the extent of about $\frac{2}{10000}$ of its volume, and that the air of cities and the country contain hydrocarbons which are probably derived from combustion processes, fermentation processes, and from the earth. The results indicate that, while methane occurs in considerable quantity, other hydrocarbons are also present, and the following table gives the number of cubic centimeters of the combustible gases contained in 100 liters of city air. These quantities are, however, subject to variations due to local conditions:

Free hydrogen	19.4
Methane	12.1
Benzene	1.7
Carbon monoxide	0.2

While the amounts of oxygen, carbon dioxide, and nitrogen are about constant, owing to the changes taking place in animal and plant life, the amount of hydrogen and methane seems to be steadily increasing. He points out that these gases are present in volcanic gases and that, while much of it is burned under ordinary conditions, when the action takes place under the sea the gases are cooled and escape unchanged. Volcanic action has been going on for ages, and all solid rocks show evidence of such action, as they contain the gaseous products in cavities of the rocks. When granite is pulverized and heated, or sometimes treated with water and acid, a considerable volume of gas is obtained which consists of carbon dioxide, hydrogen sulphide, methane, hydrogen, and several others. Even water alone will set free a large amount of gas if the temperature is raised to 280° to 300° C. Gautier considers that, in the cooling of the constituents of the earth,

compounds were formed which are unstable, and that, if we could investigate the composition of the interior of the earth, we should find sulphides, nitrides, carbides, fluorides, phosphides, etc., which by decomposition with water would form the gases actually observed in volcanic gases.

There are several methods by which the origin of the hydrogen can be explained: (*a*) By the decomposition, at red heat, of water by ferrous salts; (*b*) by the decomposition, by heat, of the hydrocarbons formed from carbides; and (*c*) in small quantity, by the decomposition of such a compound as iron nitride; thus: $N_2Fe_6 + 6H_2O = 2NH_3 + 6FeO + 6H$, a reaction which has been observed when a crystalline nitride of iron found in Etna lava was treated with water.

These and other substances are present in small quantities in rocks and are decomposed by the water which penetrates the rocks with the formation of methane, petroleum, hydrogen, etc. These gases slowly pass upward and, while the acid and active gases probably react with some substances with which they come in contact, the inactive ones finally escape from the surface. Although hydrogen is constantly being set free, an explanation of the small quantity present in the atmosphere may perhaps be due to the same cause that has been assigned by Johnstone Stoney to explain the absence of helium in quantity, its escape into interplanetary space on account of its great velocity. J. E. G.

REVIEWS.

AIR, WATER, AND FOOD FROM A SANITARY STANDPOINT. By ELLEN H. RICHARDS AND ALPHEUS G. WOODMAN, Instructors in Sanitary Chemistry, Massachusetts Institute of Technology. First edition. New York: John Wiley & Sons. 1900.

Designed as a manual for college study, this book fulfils its purpose admirably. Thirty-two pages are given to air, its impurities, ventilation, and analytical methods. Eighty pages are given to water, 100 pages to food. The better analytical methods are clearly described. Excellent tables of food values, of analyses of normal and polluted waters, etc., and a list of the more important books on the subject, enhance the value of this manual.

A quotation will show the interesting way in which Mrs. Richards writes: "The sophists were educated and intelligent men, and persuaded the people by specious reasoning. The modern 'pure food' manufacturer is a sophist who, with great skill and by the aid of the well-paid experts, persuades the general public that he is their benefactor in that his chemists have penetrated nature's secrets, hidden from the ordinary

man, and therefore that he is able to offer them long life and prosperity at so many cents to the pound..... To adulterate the coin of the realm or the liquor of the bar with a baser metal or an imitation whiskey is a heinous offense..... But the 'wretched sophistry' which obscures the nature of things on a package of prepared food misleads more persons and inflicts more injury on the community than the other, and yet goes unrebuked..... This craving for something new to stimulate a jaded appetite already spoiled by endless variety and bad combinations has led to the manufacture of a cereal preparation for nearly every day in the year.....

"The excessive fear of indigestible food which prevails among the wealthier classes may lead to universal debility of the intestinal muscular walls.[1] This fear and the lack of exercise is working mischief especially among students."

If space permitted, the reviewer would give further quotations to show the authors keen common sense. E. R.

EVOLUTION OF THE THERMOMETER: 1592–1743. By HENRY CARRINGTON BOLTON. Easton, Pa.: The Chemical Publishing Co. 1900. 98 pp. Price, $1.00.

This interesting little book contains much curious information. Its author is careful to call attention to the many steps that had to be taken before the crude open air-thermometer or, rather, thermoscope, of the age of Galileo—an instrument with no scale or with an entirely arbitrary one—should be developed into the closed mercury or alcohol thermometer of Celsius, provided with a scale based upon two clearly defined "fixed points." Many distinguished men of science participated in bringing about this progress; in addition to the names of Fahrenheit, Rèaumur, and Celsius, so generally associated with the development of thermometry, it is interesting to hear of the contributions made by Galileo, the Florentine Academy, Boyle and Newton—to mention but a few.

The principal steps in this development were (1) the adoption of a scale of degrees for making comparisons of temperatures; (2) the substitution of a closed thermometer for one subject to variations on account of changes in atmospheric pressure; (3) the adoption of alcohol and of mercury as the substances whose expansion and contraction serve as a measure of changes of temperature; (4) the realization of the advantages of a scale having clearly defined "fixed points;" (5) the choice of the boiling-point of water at standard pressure and of the melting point of ice as the fixed points of the scale.

The temptation to quote at some length is a great one, but space is wanting. It is to be hoped that many will avail themselves of the benefits offered by Dr. Bolton's careful piece of historical research. W. W. R.

[1] Bunge: "Physiological Chemistry."